THIRD EDITION

VOLUMETRIC ANALYSIS

FOR

STUDENTS OF PHARMACEUTICAL AND GENERAL CHEMISTRY

BY

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PREFACE

TO THIRD EDITION

In this edition the plan of the previous issues has been adhered to, and the scope of the book remains about the same. Some new determinations have been added, and the section on indicators has been extended.

The same arrangement of the matter has been adopted, with the object of presenting, in the first place, a general introductory course in volumetric analysis, and, in the second place, an additional specialised course suitable, during the first part of their training, for students of pharmacy or analytical chemistry.

The sections in large type include the principal standard methods, and will, it is hoped, enable the student to proceed to the use of larger works on special branches.

The sections in small type are based mainly on the requirements of the British Pharmacopœia, but some of the determinations of that work are more suitable for advanced students and have not been included.

C. H. H.

January, 1921.

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VOLUMETRIC ANALYSIS

CHAPTER I

INTRODUCTORY

The operations of quantitative analysis are usually based upon the fact that the substance to be determined undergoes in a quantitative manner some chemical change which can be expressed by an equation, from which the result is calculated. For instance, if it is desired to find the proportion of silver in an alloy of copper and silver, use is made of the fact that silver chloride is insoluble in water, while cupric chloride is soluble.

A weighed quantity of the alloy is dissolved in nitric acid, and excess of hydrochloric acid is added.

In this way the silver is precipitated quantitatively as chloride, while the copper remains in solution. The silver chloride is collected, washed free from adhering solution, dried and weighed. *All* the silver originally present is obtained finally as chloride.

Ag	becomes	AgCl.
108 grammes	give	143·5 grammes.

It is evident, therefore, that each 0·1435 gramme of silver chloride finally weighed corresponds to 0·108 gramme of silver in the amount of alloy weighed out,

and the data necessary for calculating the proportion of silver in the alloy are thus known.

The only quantitative measurement in such an analysis is that of weighing, and the process is described as *Gravimetric.*

Instead of weighing the silver chloride, the quantity of hydrogen chloride necessary to precipitate the silver may be found, and the result calculated from the equation

$$AgNO_3 + HCl = AgCl + HNO_3$$

HCl corresponds to	$AgNO_3$	or	Ag.
36·5 grammes	170 grammes		108 grammes :

therefore for each 0·365 gramme of hydrochloric acid added, 1·08 gramme of silver would be present in the quantity of alloy taken.

The simplest method of finding out how much hydrochloric acid is necessary to precipitate the silver is to add a solution of known strength until the precipitation is complete, then to measure the volume of solution added. This process is called *Titration.* Analytical operations of this kind, involving the measurement of volumes, are described as *Volumetric.*

A solution of which the strength is accurately known is called a *Standard Solution.*

A *Normal Solution* is one which contains in 1,000 c.c., that weight of the active substance which is chemically equivalent to 1 gramme of hydrogen.

Hydrochloric acid, HCl, contains one atom of hydrogen in the molecule, *i.e.*, 1 gramme of hydrogen in each 36·5 grammes, and a normal solution will therefore contain 36·5 grammes, the gramme-molecular weight, of hydrochloric acid, in 1,000 c.c.

Sulphuric acid contains two atoms of hydrogen in the molecule, and a normal solution therefore contains 49 grammes, half the gramme-molecular weight, in 1,000 c.c.

In deducing the weight of any substance which is equivalent to 1 gramme of hydrogen, it is necessary to consider the nature of the reaction for which the substance is to be used.

The equation

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$

shows that one molecule of sodium carbonate is equivalent to two molecules of hydrochloric acid, and therefore half the gramme-molecular weight of sodium carbonate is equivalent to 1 gramme of hydrogen.

Similarly, from the equations

$$NaOH + HCl = NaCl + H_2O\,;$$

$$NaOH + CH_3COOH = CH_3COONa + H_2O,$$

it is clear that a normal solution of sodium hydroxide or acetic acid will contain the gramme-molecular weight in 1,000 c.c.

It should be noted in the case of acetic acid that although there are four hydrogen atoms in the molecule, only one exercises the acid function, and therefore the gramme-molecular weight is equivalent to 1 gramme of hydrogen.

Normal solutions are indicated by the capital letter N.

For some determinations, solutions weaker than normal are required, and seminormal (N/2), decinormal (N/10), and centinormal (N/100) solutions are commonly used. These are respectively one-half, one-tenth, and one-hundredth the strength of a normal solution.

It is evident from the above explanation that equal volumes of normal solutions are equivalent to one another. For example, 1 c.c. of N. hydrochloric acid will exactly neutralise 1 c.c. of N. sodium hydroxide solution or 10 c.c. of N/10 sodium carbonate solution, and so on. This fact is often of great service in simplifying calculations, and examples of its use will occur later.

CHAPTER II

ACIDIMETRY AND ALKALIMETRY

Normal Sodium Carbonate Solution.

Standard solutions of sodium carbonate are readily prepared by dissolving the requisite amount of the pure anhydrous salt in water and diluting to the required volume.

The molecular weight of sodium carbonate, Na_2CO_3, is 106 and, therefore, 1,000 c.c. of a normal solution contain 53 grammes.

Pure anhydrous sodium carbonate is best prepared by heating the pure bicarbonate, which is thereby decomposed according to the equation

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

Weigh out about 100 grammes of pure sodium bicarbonate in a porcelain dish and heat over the bunsen flame, so that the bottom of the dish is a dull red, for about twenty minutes, taking care not to fuse the salt. Allow the sodium carbonate to cool in a desiccator, weigh out 53 grammes, place in a 1,000 c.c. flask, add water, shake until dissolved, then fill up the flask to the mark on the neck.

The dish must not be heated too strongly or some sodium carbonate may be decomposed with formation of the hydroxide. If fusion takes place, the glaze on the

dish may be attacked and sodium silicate formed. Any fused portions of the product should be rejected.

Anhydrous sodium carbonate readily takes up moisture from the air ; hence it is better to cool the product in a desiccator.

Since a contraction in volume takes place when sodium carbonate dissolves in water, the final volume of the solution should not be adjusted until all the salt has dissolved.

Normal Sulphuric Acid Solution.

A solution of approximately N. strength is prepared by diluting the concentrated acid and the strength is ascertained accurately by comparison with the N. sodium carbonate solution.

Forty-nine grammes of pure H_2SO_4 are required. Commercial samples of concentrated sulphuric acid usually contain about 95 per cent. of H_2SO_4 and have a specific gravity of about 1·8 ; hence about 50 grammes or 28 c.c. may be taken.

Measure out 28 c.c. of concentrated sulphuric acid and add it slowly to about 500 c.c. of water contained in a 1,000 c.c. flask. Shake well, cool and make up to 1,000 c.c.

Standardisation of the Sulphuric Acid Solution.

In order to arrive at the strength of the sulphuric acid solution thus prepared, it is necessary to ascertain what volume will exactly neutralise a definite volume of the N. sodium carbonate solution.

The alkali solution is measured with a pipette into a titrating flask and the acid solution is added from a

burette until the liquid is exactly neutral. The volume of acid solution is then read off. No change takes place in the appearance of the solution when the point of neutralisation is reached and it is necessary to add to the liquid in the flask some substance which, by a change of colour, shows when the acid has been added in sufficient quantity to neutralise the alkali. Such a substance is called an *Indicator*. The most suitable indicator in the present case is methyl orange, which in alkaline solution is yellow, and in acid solution, red. If the indicator is properly used the change from yellow to red is very sharp and the addition of the acid can be controlled with great accuracy.

Take 20 c.c. of the N. sodium carbonate solution, add sufficient methyl orange solution to produce a *pale yellow* colour, and titrate with the sulphuric acid solution until the liquid just becomes pink. The strength of the sulphuric acid solution is then calculated from the equation

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O.$$

$Na_2CO_3 \quad = H_2SO_4 \quad = 2H.$

106 grammes = 98 grammes = 2 grammes.

53 ,, = 49 ,, = 1 gramme = 1,000 c.c. N. sol.

0·053 gramme = 0·049 gramme = 1 c.c. N. solution.

Each c.c. of N. sodium carbonate solution requires for neutralisation 0·049 gramme of H_2SO_4.

Suppose that 20 c.c. of N. sodium carbonate solution required 19·5 c.c. of sulphuric acid solution.

Then 19·5 c.c. of sulphuric acid solution contain $20 \times 0{\cdot}049$ gramme of H_2SO_4 and 1,000 c.c. contain

$$\frac{20 \times 0{\cdot}049 \times 1{,}000}{19{\cdot}5} = 50{\cdot}26 \text{ grammes of } H_2SO_4.$$

Instead of calculating the strength of the sulphuric acid solution, we may convert it into a N. solution. Since 19·5 c.c. are equivalent to 20 c.c. of N. solution, it is only necessary to dilute 19·5 c.c. to 20 c.c. or 975 c.c. to 1,000 c.c. in order to obtain a solution of exactly normal strength.

The process of measuring and diluting may involve a slight error if the measuring vessels are not strictly correct, and it is preferable to avoid this inaccuracy by calculating the "Factor" of the solution in the following way:—

Since 19·5 c.c. of sulphuric acid sol. $= 20$ c.c. of N. sol.

$\therefore$ 1 ,, ,, ,, ,, $= \dfrac{20}{19 \cdot 5}$,, ,,

$= 1 \cdot 026$,, ,,

It is evident that the volume of N. solution equivalent to any volume of the sulphuric acid solution used subsequently in a titration, is obtained by multiplying by the factor 1·026. The advantages attaching to the use of normal solutions are thus obtained without the trouble and possible inaccuracy of diluting the solution.

CHAPTER III

INDICATORS—SOURCES OF ERROR

THE indicators used in acidimetry and alkalimetry are acidic or basic in character, and their use depends upon the difference in colour between solutions of the free acid or base and of its salts. The acid of methyl orange has a red colour, and the salts are yellow. In the titration of an alkali such as sodium hydroxide with sulphuric acid the yellow colour of the sodium salt is obtained when the indicator is added to the alkali solution in the flask. On running in the acid the sodium salt of methyl orange is unaffected so long as any sodium hydroxide remains undecomposed, but the addition of the slightest excess of acid causes the liberation of the free acid of methyl orange and the solution becomes red. If the titration is carried out in the reverse way, the alkali being added to the acid, the solution in the flask shows the red colour so long as any free sulphuric acid is present. The addition of the least excess of sodium hydroxide over the amount required to neutralise the sulphuric acid results in the formation of the yellow sodium salt of methyl orange.

A large number of colouring matters, some of vegetable or animal origin, others synthetic products of the laboratory, are available for use as indicators. One or

other of those now to be described will be found suitable for all the determinations of acids and alkalis. It is important that the student should learn the advantages and disadvantages of each and the determinations for which they may be used with success. A little practice is necessary to accustom the eye to judging the colour change, and it is best to observe the same change of colour in all titrations with any particular indicator. The acid may be added to the alkali or *vice versâ*, but the procedure should be the same in all titrations. It is usual to work with the acid in the burette, since solutions of alkalis affect glass more readily and are apt to cause the tap to stick.

Methyl Orange is the sodium or ammonium salt of para-dimethylamino-azobenzenesulphonic acid

$$(CH_3)_2N.C_6H_4.N = NC_6H_4SO_2OH.$$

It occurs as an orange-yellow powder which is slightly soluble in cold water and almost insoluble in alcohol. A 0·1 per cent. aqueous solution forms a convenient liquid for use as an indicator. It is readily decomposed by strong mineral acids, and it is most suitable for titrations in which they are concerned. It is not affected by feeble acids such as carbonic acid, hydrocyanic acid, hydrogen sulphide, or boric acid, and can be used in presence of these acids to indicate the neutralisation of a mineral acid. It is therefore the most suitable indicator in the determination of carbonates or borax. Methyl orange is only partly decomposed by organic acids and cannot be used to indicate their neutralisation. It gives satisfactory results in ammonia titrations.

The sensitiveness of this indicator is greatly diminished if too much is used; sufficient should be

used to give only a *pale yellow* colour to the alkali solution.

Methyl Red is para-dimethylamino-azobenzene-ortho-carboxylic acid

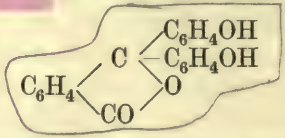
$$(CH_3)_2N.C_6H_4.N = NC_6H_4COOH.$$

It forms violet crystals which are very slightly soluble in cold water but readily soluble in alcohol. A 0·2 per cent. solution in alcohol is used. In alkaline solution it has a bright yellow colour, in slightly acid solution a rose-red colour, and in strongly acid solution a violet-red colour. It is a more sensitive indicator than methyl orange and the colour change is sharper. This advantage is especially notable when working with very dilute solutions. It is, however, sensitive to carbon dioxide. Methyl red may replace methyl orange in all cases except that in the titration of carbonates the solution must be kept boiling to expel the carbon dioxide formed.

Litmus is a plant extract obtained from *Rocella tinctoria.* The principal colouring constituent is azolitmin, which behaves like a weak acid and has a red colour. The alkali salts of azolitmin are blue. It is soluble in water but insoluble in alcohol. The solution for use as indicator is prepared by exhausting the crude material with three successive quantities of boiling alcohol for one hour each (to remove another colouring matter, erythrolitmin), digesting the residue in cold water and filtering. Litmus is used in the titration of mineral acids and is suitable also for oxalic, lactic and tartaric acids, but for other organic acids it is not a trustworthy indicator. It is sensitive to carbonic acid, and if used in the titration of carbonates the red colour is obtained before all the carbonate is decomposed. This difficulty

is surmounted by boiling the liquid to expel the carbon dioxide. Boric acid affects litmus to some extent, and this indicator is therefore not suitable for the titration of borax. It gives good results in ammonia titrations.

Phenol-phthalein, or dihydroxy-diphenyl-phthalide,



is a colourless, finely-crystalline substance which is almost insoluble in water but readily soluble in alcohol. The neutral or acid solution is colourless, but in presence of alkali a deep red salt is formed. A 1 per cent. solution in alcohol may be used. The alkali salts are very readily decomposed by weak acids, and phenol-phthalein is therefore the most suitable indicator in the titration of an organic acid with an alkali hydroxide, the end-reaction being very sharply marked. Since the alkali salts are decomposed by carbonic acid, this indicator is not used in the titration of carbonates unless it is necessary to titrate a carbonate with an organic acid. In this case the solution must be boiled to expel carbon dioxide. Phenol-phthalein does not give reliable indications in titrations of ammonia, or of alkalis in presence of ammonium salts.

Cochineal consists of the dried female insect *Coccus cacti*. The colouring substance, carminic acid, is soluble in water or alcohol and has a yellowish-red colour, which is changed to violet by alkalis. A 10 per cent. alcoholic tincture of the crude cochineal may be used. It is a suitable indicator in the titration of alkalis, alkaline earths, ammonia, and certain alkaloids with mineral

acids. It does not give reliable indications with organic acids. It is slightly affected by carbonic acid and cannot be used in presence of acetates or compounds of iron or aluminium.

For determinations other than titrations of acids and alkalis certain other indicators are used, and these will be described later in connection with the determinations for which they are used. In some cases no indicator is necessary.

The causes which influence the accuracy of the results obtained in volumetric analysis may be dealt with under three headings: (*a*) Errors due to the nature of the reaction employed; (*b*) Errors in the measuring vessels and weights; (*c*) Errors in manipulation.

(*a*) It has been stated already that quantitative analysis is usually based upon some chemical change which can be carried out in a quantitative manner. Most of the reactions used in volumetric analysis rigidly fulfil this condition, but in certain cases the change is not perfectly quantitative or is only made so under special conditions. For instance, the determination of calcium, described on p. 50, depends on the precipitation of calcium as carbonate by means of sodium carbonate. This precipitation is complete only when the liquid is heated nearly to boiling and allowed to cool before filtering. If this condition is not fulfilled some calcium remains in solution and an error is introduced. The determination of chloral hydrate, described on p. 53, provides an instance where an error is introduced by the occurrence of a secondary reaction. The degree of accuracy required in the analysis must also be considered. In the determination of chlorides by means of

standard silver nitrate solution where the end-point is recognised by the cessation of precipitation, a slight error is introduced owing to the solubility of silver chloride. This error is so slight as to be negligible in ordinary volumetric analysis, but when this process is employed in the determination of atomic weights it becomes of importance and a correction must be applied.

(*b*) The measuring vessels used should correspond exactly with one another, *i.e.*, the volume of liquid delivered by the 10 c.c. pipette should exactly fill 10 c.c. in any part of the burette; five times the volume of liquid delivered by the 20 c.c. pipette should fill the 100 c.c. flask precisely to the mark on the neck; the 1,000 c.c. flask should hold exactly twice the volume measured by the 500 c.c. flask, and so on. The absolute accuracy of the measuring vessels is of no consequence so long as this correspondence is attained. The weights used should correspond among themselves in a similar way.

(*c*) The measuring vessels should be perfectly clean. It is not possible to read the level of the liquid correctly if the interior of the vessel is not clean.

Pipettes should be filled by suction to the mark on the stem; the liquid should then be allowed to run into the flask and the point of the pipette finally touched against the side of the flask. Used in this way a clean correctly-graduated pipette *delivers* exactly the stated volume. A drop of liquid remains in the point of the pipette, and this must not be expelled by blowing. If the interior of the pipette is not clean small drops of liquid remain upon the glass and a corresponding error is introduced. Inaccuracies result if the change in the indicator is not correctly noted; the addition of a drop

in excess or deficiency of the right amount may make an appreciable difference in the result. The readings obtained with a particular indicator are not always the same when made by artificial light as when the titration is done in daylight. The change of colour in methyl orange is much more easily seen by daylight than by artificial light; the reverse is the case with the potassium chromate indicator for silver titrations.

The level of the liquid in the burette before and after each titration must be carefully read, the same point on the meniscus being taken in each case. Before taking the reading the burette must be allowed to stand for at least half a minute to allow the liquid to run down from the sides.

The influence of the causes mentioned under (*c*) is evidently diminished by using dilute solutions and in large volumes. As a rule pipettes of smaller capacity than 10 c.c. should not be used and it is preferable to employ 20 c.c. pipettes. The strengths of the solutions should be so arranged that about 15 to 20 c.c. will be delivered from the burette in each titration. These points must be considered when calculating how much of the sample under test is to be weighed out and what strength of standard solution is to be used.

Whenever possible the titration should be repeated twice and the burette readings should not differ by more than 0·1 c.c. In the instructions for most of the determinations mentioned in the following pages the student is directed to prepare 100 c.c. of a solution of the substance. This allows of the titration being repeated several times. The work should be checked by a second weighing whenever time allows.

The variation of the volume of the solutions with change of temperature may cause inaccuracy. Volumetric apparatus is usually standardised at 15·5° C., the average room temperature, and errors are introduced if the solutions are used at temperatures different from this. Some substances, when dissolved in water, cause the evolution of heat, others bring about its absorption, and a solution, when freshly prepared, may differ by several degrees from the laboratory temperature. When preparing solutions, therefore, the final adjustment of volume must not be made until all the substance has dissolved and the solution has assumed the temperature of the surrounding air.

CHAPTER IV

ACIDIMETRY AND ALKALIMETRY (*continued*)

Determinations with Sulphuric Acid.

WHEN the preliminary work described in Chapter II. has been completed the alkalimetric determinations may be undertaken. As an example the purity of sodium carbonate crystals, $Na_2CO_310H_2O$, may be determined. From the equation on p. 7.

$Na_2CO_3.10H_2O$	$= H_2SO_4$	$= 2H$.
286 grammes	= 98 grammes	= 2 grammes.
143 ,,	= 49 ,,	= 1,000 c.c. N. sol.
0·143 gramme	= 0·049 gramme	= 1 c.c. ,, ,,

Assuming the crystals to contain only small amounts of impurities,* it is evident that about 14·3 grammes dissolved in sufficient water to produce 100 c.c. will form a solution of convenient strength for titration with N. sulphuric acid. About 14·3 grammes of the sample should be weighed out and dissolved in water and the solution made up to 100 c.c.; 20 c.c. should then be titrated with N. sulphuric acid as already described on p. 7. The result is calculated as shown in the following example :—

* For pharmaceutical purposes the salt should contain at least 99 per cent. of $Na_2CO_3.10H_2O$.

14·1 grammes of the crystals were dissolved in water and the solution diluted to 100 c.c.

20 c.c. required (1) 19·7, (2) 19·6, (3) 19·6 c.c. N. H_2SO_4.

1 c.c. N. H_2SO_4 neutralises 0·143 gramme of pure $Na_2CO_3.10H_2O$.

$\therefore$ 19·6 c.c. neutralise 2·8028 grammes of pure $Na_2CO_3.10H_2O$.

$\therefore$ 20 c.c. of sodium carbonate solution contain 2·8028 grammes of pure $Na_2CO_3.10H_2O$.

$\therefore$ 100 c.c. (14·1 grammes of sample) contain 14·014 grammes.

$\therefore$ 100 grammes of sample contain $\dfrac{14{\cdot}014 \times 100}{14{\cdot}1} =$

99·4 grammes of pure $Na_2CO_310H_2O$.

The student should realise that the essential point here is that the strength of the sulphuric acid is accurately known; the use of the solution of the strength designated normal is a convenience in many cases, as will be seen later, but here it has no particular advantage. To emphasise this point, the determination may be repeated with sulphuric acid of some other strength. For example, a solution containing exactly 0·03 gramme H_2SO_4 per c.c. may be used. Since

0·049 gramme H_2SO_4 neutralises 0·143 gramme $Na_2CO_310H_2O$,

$\therefore$ 0·03 gramme H_2SO_4 neutralises $\dfrac{0{\cdot}143 \times 0{\cdot}03}{0{\cdot}049} =$

0·08755 gramme $Na_2CO_310H_2O$.

About 8·7 grammes of the crystals dissolved in sufficient water to produce 100 c.c. therefore form a solution of suitable strength for the titration.

The purity of the crystals is calculated as in the following example :—

8·52 grammes of the sample were dissolved in water and the solution diluted to 100 c.c.

20 c.c. required (1) 19·4, (2) 19·3, (3) 19·3 c.c. of standard sulphuric acid containing 0·03 gramme H_2SO_4 per c.c.

20 c.c. contain ·08755 × 19·3 gramme of pure $Na_2CO_310H_2O$.

100 c.c. (8·52 grammes of sample) contain 8·4679 grammes of pure $Na_2CO_310H_2O$.

$\therefore$ 100 grammes of sample contain $\dfrac{8{\cdot}4679 \times 100}{8{\cdot}52} =$ 99·4 grammes of pure $Na_2CO_310H_2O$.

Throughout the book the quantities to be taken for the various determinations are given for convenience, but the student should verify these from the equations and from a knowledge of the probable composition of the material analysed, and should practise making the determinations with standard solutions of strengths other than normal or decinormal, as indicated in the second example above.

Ammonia.

The strength of a solution of ammonia is found by titration with standard acid.

According to the equation

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

$$2NH_3 = H_2SO_4 = 2H.$$

34 grammes	= 2 grammes.	
17 ,,	= 1 gramme =	1,000 c.c. N. sol.
0·017 gramme	=	1 c.c. ,, ,,

For practice determine the ammonia in the bench reagent which contains 5 to 7 per cent.

Weigh out about 20 grammes of the solution in a stoppered bottle and dilute to 100 c.c. Titrate 20 c.c. of the diluted solution with N. sulphuric acid, using methyl orange or cochineal as indicator.

The result obtained by direct titration in this way is liable to come out too low owing to the volatilisation of ammonia during the titration. This error is avoided if the process of " back titration " is employed (*see* p. 47).

Soda-ash.

Soda-ash consists chiefly of anhydrous sodium carbonate with some sodium hydroxide. Water and other impurities are also present. The student should determine the proportions of carbonate and hydroxide present and also the total alkali calculated as sodium oxide, Na_2O.

Determination of Carbonate and Hydroxide.—The reactions taking place on the addition of sulphuric acid are expressed by the equations

(1) $2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$.

(2) $Na_2CO_3 + H_2SO_4 = Na_2SO_4 + CO_2 + H_2O$.

The latter reaction takes place in two stages, thus :—

(3) $2Na_2CO_3 + H_2SO_4 = Na_2SO_4 + 2NaHCO_3$.

(4) $2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2CO_2$.

If the soda-ash is titrated with sulphuric acid, using phenol-phthalein as indicator, the colour is discharged when reactions (1) and (3) are complete, because the carbon dioxide evolved immediately reaction (4) begins decolorises this indicator. If now methyl orange is added, the alkaline colour is obtained because this

indicator is not sensitive to carbonic acid, and the pink colour is not obtained until sufficient acid has been added to neutralise both hydroxide and carbonate. The reading with phenol-phthalein is the acid required to neutralise the hydroxide plus half that required by the carbonate. The difference between the two readings represents half the acid required by the carbonate. The weak point of the method is that any loss of carbon dioxide during the first part of the titration makes the phenol-phthalein reading too high. To avoid this loss the solution must be kept cool, the point of the burette should dip below the surface of the liquid, and the liquid should be stirred all the time.

Weigh out about 8 grammes of the sample and dissolve it in sufficient water to produce 100 c.c. Measure 20 c.c., add a drop of phenol-phthalein solution and titrate with N. sulphuric acid until the colour disappears. Read the burette, add methyl orange, and titrate again until the solution becomes pink. Again read the burette.

From the equations given

$Na_2CO_3 = H_2SO_4 = 2H.$

106 grammes = 2 grammes.

53 ,, = 1 gramme = 1,000 c.c. N. sol.

0·053 gramme = 1 c.c. ,, ,,

and $2NaOH = H_2SO_4 = 2H.$

80 grammes = 2 grammes.

40 ,, = 1 gramme = 1,000 c.c. N. sol.

0·04 gramme = 1 c.c. ,, ,,

Example.—7·98 grammes of the sample were dissolved in water and diluted to 100 c.c.

20 c.c. required (1) 15·4, (2) 15·3, (3) 15·3 c.c. N. H_2SO_4
Indicator Phenol-Phthalein.

20 c.c. „ (1) 28·5, (2) 28·4, (3) 28·4 c.c. N. H_2SO_4
Indicator Methyl Orange.

$\therefore$ 28·4 − 15·3 c.c. = 13·1 c.c. N. H_2SO_4 = half the acid required to neutralise the carbonate in 20 c.c. of the solution.

$\therefore$ the carbonate in 20 c.c. requires 26·2 c.c. N. H_2SO_4
and the hydroxide „ „ „ 28·4 − 26·2 = 2·2 c.c. N. H_2SO_4.

20 c.c. of the solution contain $0{\cdot}053 \times 26{\cdot}2$ grammes of Na_2CO_3.

100 c.c. „ „ (7·98 grammes of the sample) contain $0{\cdot}053 \times 26{\cdot}2 \times 5$ grammes of Na_2CO_3.

$$\therefore \text{ 100 grammes of sample contain } \frac{0{\cdot}053 \times 26{\cdot}2 \times 5 \times 100}{7{\cdot}98}$$

= 87 grammes of anhydrous sodium carbonate.

20 c.c. of solution contain $0{\cdot}04 \times 2{\cdot}2$ grammes of NaOH.

100 c.c. „ „ (7·98 grammes of sample) contain $0{\cdot}04 \times 2{\cdot}2 \times 5$ grammes of NaOH.

$$\therefore \text{ 100 grammes of sample contain } \frac{0{\cdot}04 \times 2{\cdot}2 \times 5 \times 100}{7{\cdot}98}$$

= 5·51 grammes of sodium hydroxide.

Determination of Total Alkali.—The total alkali in the sample is calculated from the methyl orange reading in the last titration.

According to the equation

$$Na_2O + H_2SO_4 = Na_2SO_4 + H_2O.$$

$Na_2O = H_2SO_4 = 2H.$
62 grammes $= 2$ grammes.
31 ,, $= 1$ gramme $= 1{,}000$ c.c. N. sol.
0·031 gramme $=$ 1 c.c. ,, ,,

Example.—From the above results
The total alkali in 20 c.c. required 28·4 c.c. N. H_2SO_4.
,, ,, ,, 100 c.c. (7·98 grammes of sample) required $28{\cdot}4 \times 5$ c.c.

$$\therefore \text{100 grammes of sample contain } \frac{28{\cdot}4 \times 5 \times 0{\cdot}031 \times 100}{7{\cdot}98}$$
$$= 55{\cdot}16 \text{ grammes of } Na_2O.$$

Sodium Carbonate and Bicarbonate.

The proportions of carbonate and bicarbonate in a mixture may be determined by titration with standard acid, using the two indicators just as in the determination of sodium hydroxide and carbonate in soda-ash. In this case the solution will be acid to phenol-phthalein when half the acid necessary to neutralise the carbonate has been added. The difference between twice this reading and the total amount of acid added gives the acid necessary to neutralise the bicarbonate.

From the equations already given
$Na_2CO_3 = H_2SO_4 = 2H.$
106 grammes $= 2$ grammes.
53 ,, $= 1$ gramme $= 1{,}000$ c.c. N. sol.
0·053 gramme $=$ 1 c.c. ,, ,,
$2NaHCO_3 = H_2SO_4 = 2H.$
168 grammes $= 2$ grammes.
84 ,, $= 1$ gramme $= 1{,}000$ c.c. N. sol.
0·084 gramme $=$ 1 c.c. ,, ,,

For practice find the proportions of sodium carbonate and bicarbonate in sodium sesquicarbonate,

$$Na_2CO_3 2NaHCO_3 2H_2O.$$

Weigh out 9 grammes of the substance and dissolve in sufficient water to make 100 c.c. Titrate 20 c.c. with N. H_2SO_4, using first phenol-phthalein and then methyl orange as indicator, with the precautions mentioned under soda-ash.

Borax.—Sulphuric acid decomposes borax according to the equation

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = Na_2SO_4 + 4H_3BO_3.$$

The purity of borax may be found by titration with standard acid if methyl orange, which is not affected by boric acid, is used as indicator.

From the above equation

$Na_2B_4O_7.10H_2O = H_2SO_4 = 2H.$
382 grammes = 2 grammes.
191 ,, = 1 gramme = 1,000 c.c. N. sol.
0·0191 gramme = 1 c.c. N/10 ,,

Take 1·5 grammes of the sample and dissolve in sufficient water to make 100 c.c. Titrate 20 c.c. with N/10 sulphuric acid, using methyl orange as indicator.

The result obtained by this method of titration is liable to error, since borax may contain alkaline impurities. A determination of the boric acid liberated, using the method described on p. 39, should be made as a check.

The purified borax of pharmacy should contain at least 98·9 per cent. of the hydrated salt, $Na_2B_4O_7.10H_2O$.

Lime Water.—This preparation is a saturated aqueous solution of calcium hydroxide. The strength is determined by titration with standard acid and is usually expressed in terms of lime, CaO.

According to the equation

$CaO + H_2SO_4 = CaSO_4 + H_2O.$
$CaO = H_2SO_4 = 2H.$
56 grammes = 2 grammes.
28 ,, = 1 gramme = 1,000 c.c. N. solution.
0·0028 gramme = 1 c.c. N/10 ,,

Titrate 25 c.c. of the sample with N/10 sulphuric acid, using methyl orange as indicator.

1,000 c.c. should contain the equivalent of rather more than 1 gramme of CaO.

Saccharated Solution of Lime.—This preparation is made by dissolving calcium hydroxide in a solution of cane-sugar. The calcium hydroxide and the sugar combine to form a compound, calcium saccharosate, which is more soluble than calcium hydroxide. The lime so combined reacts in the usual way with acids, and the amount present is found by titration with standard acid as for lime water. The organic matter present renders the end-point with methyl orange uncertain, and phenol-phthalein should be used as indicator.

Take 20 c.c. of the sample and titrate with N. sulphuric acid, using phenol-phthalein as indicator.

The solution should contain nearly 2 per cent. of CaO.

Strong Solution of Ammonia and Solution of Ammonia.—These solutions should contain respectively 32·5 and 10 per cent. of ammonia. The strength is determined as described on p. 19.

Ammonium Carbonate.—Commercial ammonium carbonate is a variable mixture of ammonium carbamate $CO(NH_2)(ONH_4)$ and ammonium hydrogen carbonate $CO(OH)(ONH_4)$.

For pharmaceutical purposes the substance should contain at least 30·6 per cent. of total ammonia calculated as NH_3. This is determined by titration with standard acid.

Weigh out about 4 grammes and dissolve in sufficient water to produce 100 c.c. Titrate 20 c.c. of the solution with N. sulphuric acid, using methyl orange as indicator.

The reactions taking place are as follows :—

Ammonium carbonate when dissolved in water is converted into the carbonate

$$CO(NH_2)(ONH_4) + H_2O = (NH_4)_2CO_3.$$

This is neutralised by sulphuric acid thus :—

$$(NH_4)_2CO_3 + H_2SO_4 = (NH_4)_2SO_4 + H_2O + CO_2.$$

The ammonium hydrogen carbonate is neutralised according to the equation

$$2NH_4HCO_3 + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O + 2CO_2.$$

Fetid Spirit of Ammonia.—This preparation consists of a mixture of strong solution of ammonia with an alcoholic solution of the volatile principles of asafetida. The ammonia is determined by means of

standard acid. Titrate 10 c.c. with N. sulphuric acid, using methyl orange as indicator.

100 c.c. should contain at least 2·72 grammes of ammonia NH_3.

Aromatic Spirit of Ammonia.—This preparation is a solution of ammonia and ammonium carbonate in diluted alcohol containing flavouring agents. The total ammonia present, calculated as NH_3, is found by titration with standard acid.

Take 20 c.c. and titrate with N. sulphuric acid, using methyl orange as indicator.

100 c.c. should contain 2·16 grammes of ammonia, NH_3.

The determination of the ammonium carbonate present is described on p. 51.

Potassium Hydroxide.—The proportion of pure potassium hydroxide in the commercial substance is found by titration with standard acid.

According to the equation

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O.$$
$$2KOH = H_2SO_4 = 2H.$$
$$112 \text{ grammes} = 2 \text{ grammes}.$$
$$56 \text{ grammes} = 1 \text{ gramme} = 1{,}000 \text{ c.c. N. solution.}$$
$$\cdot056 \text{ gramme} = 1 \text{ c.c. ,, ,,}$$

Weigh out about 6 grammes of the sample in a stoppered weighing-bottle. Dissolve in sufficient water to make 100 c.c. of solution and titrate 20 c.c. with N. sulphuric acid, using methyl orange as indicator.

The official substance should contain not less than 85 per cent. of pure potassium hydroxide.

Solution of Potash.—The strength of the solution is determined in the same way as the purity of the solid substance.

Take 20 c.c., add a little methyl orange solution, and titrate with N. sulphuric acid.

100 c.c. of the solution should contain 5 grammes of pure potassium hydroxide, KOH.

Potassium Bicarbonate.—The neutralisation of potassium bicarbonate by sulphuric acid is represented by the equation

$$2KHCO_3 + H_2SO_4 = K_2SO_4 + 2CO_2 + 2H_2O,$$

whence $2KHCO_3 = H_2SO_4 = 2\text{ H}.$

$$200 \text{ grammes} = 2 \text{ grammes}.$$
$$100 \text{ ,,} = 1 \text{ gramme} = 1{,}000 \text{ c.c. N. sol.}$$
$$0{\cdot}01 \text{ gramme} = 1 \text{ c.c. N/10 ,,}$$

Weigh out about 1 gramme of the sample and dissolve in sufficient

water to produce 100 c.c. Titrate 20 c.c. with N/10 sulphuric acid, using methyl orange as indicator. Not less than 99 per cent. of the pure salt should be present.

Potassium Carbonate.—The official substance consists of potassium carbonate, associated with either one or two molecules of water. It should contain not less than 81·5 per cent. of pure potassium carbonate, K_2CO_3.

The reaction with sulphuric acid is expressed by the equation

$$K_2CO_3 + H_2SO_4 = K_2SO_4 + H_2O + CO_2,$$

whence $K_2CO_3 = H_2SO_4 = 2H$.

138 grammes = 2 grammes.
69 ,, = 1 gramme = 1,000 c.c. N. sol.
0·0069 gramme = 1 c.c. N/10 ,,

Weigh out about 0·7 gramme of the sample, dissolve in water and dilute to 100 c.c. Titrate 20 c.c. with N/10 sulphuric acid, using methyl orange as indicator.

Lithium Carbonate.—This substance is only moderately soluble in water, but it may be titrated in suspension by means of sulphuric acid. It should contain at least 98·5 per cent. of the pure salt.

From the equation

$$Li_2CO_3 + H_2SO_4 = Li_2SO_4 + CO_2 + H_2O.$$

$Li_2CO_3 = H_2SO_4 = 2H$.

74 grammes = 2 grammes.
37 ,, = 1 gramme = 1,000 c.c. N. solution.
·037 gramme = 1 c.c. ,, ,,

Weigh out 1 gramme and diffuse in about 50 c.c. of water. Titrate with N. sulphuric acid, using methyl orange as indicator.

Sodium Bicarbonate.—Sulphuric acid neutralises sodium bicarbonate according to the equation

$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2CO_2 + 2H_2O,$$

whence $2NaHCO_3 = H_2SO_4 = 2H$.

168 grammes = 2 grammes.
84 ,, = 1 gramme = 1,000 c.c. N. sol.
0·0084 gramme = 1 c.c. N/10 ,,

Weigh out about 0·8 gramme of the sample and dissolve in sufficient water to produce 100 c.c. Titrate 20 c.c. with N/10 sulphuric acid, using methyl orange as indicator.

Not less than 98·5 per cent. of the pure salt should be present.

Exsiccated Sodium Carbonate.—This is determined in the same way as the crystalline salt, and 95 per cent. of the pure anhydrous salt should be present.

About 0·5 gramme dissolved in sufficient water to produce 100 c.c. gives a suitable solution for titration with N/10 sulphuric acid.

0·0053 gramme = 1 c.c. N/10 solution.

Potassium Citrate.—The official salt is required to contain at least 99 per cent. of the hydrate $K_3C_6H_5O_7.H_2O$. When it is heated to redness, charring takes place, and on further heating most of the carbon burns away and a residue of potassium carbonate is left behind. All the potassium originally present is found finally as carbonate. By titrating the carbonate with standard acid the purity of the citrate can be found.

$2K_3C_6H_5O_7.H_2O$ yields $3K_2CO_3$,
whence $2K_3C_6H_5O_7.H_2O = 3H_2SO_4 = 6H$.
648 grammes = 6 grammes.
108 ,, = 1 gramme = 1,000 c.c. N. sol.
0·0108 gramme = 1 c.c. N/10 ,,

Weigh about 1 gramme of the sample into a crucible and heat gently until charring has taken place, keeping the crucible covered to prevent loss by spurting. Remove the cover and heat to redness for ten minutes. Dissolve the residue in 50 or 60 c.c. of hot water and filter the solution into a 100 c.c. flask. Wash out the crucible with more water, pouring the washings over the filter until the solution, after cooling to laboratory temperature, measures 100 c.c. Titrate 20 c.c. with N/10 sulphuric acid, using methyl orange as indicator.

The solution of carbonate must be colourless. If it is dark in colour the incineration is incomplete and the result obtained will be too low.

Potassium Tartrate.—The official salt is required to contain not less than 99 per cent. of the hydrate $(K_2C_4H_4O_6)_2H_2O$.

Potassium tartrate is converted into carbonate by incineration in the same way as the citrate.

$K_2C_4H_4O_6$ becomes K_2CO_3.
$(K_2C_4H_4O_6)_2.H_2O = 2H_2SO_4 = 4H$.
470 grammes = 4 grammes.
117·5 ,, = 1 gramme = 1,000 c.c. N. sol.
0·01175 gramme = 1 c.c. N/10 ,,

Take about 1 gramme and carry out the determination exactly as directed for potassium citrate.

Acid Potassium Tartrate.—The purity of cream of tartar may be determined in two ways. The first method depends on its acid property and is fully described on pp. 43, 44. The disadvantage of this method is that any other acid salt, such as potassium hydrogen

sulphate, which may be present is reckoned as acid potassium tartrate.

The second method, which is free from this disadvantage, consists in converting it into potassium carbonate by heating and titrating the residue with standard acid as directed for potassium citrate.

$2KHC_4H_4O_6$ becomes K_2CO_3.

$2KHC_4H_4O_6 = H_2SO_4 = 2H$.

376 grammes = 2 grammes.

188 ,, = 1 gramme = 1,000 c.c. N. solution.

0·0188 gramme = 1 c.c. N/10 ,,

Weigh out about 2 grammes and determine by the process described for potassium citrate. It should contain at least 99 per cent. of the pure salt.

Sodium Potassium Tartrate.—Rochelle salt should contain at least 98 per cent. of the pure hydrate $KNaC_4H_4O_64H_2O$. It is converted on incineration into a mixture of potassium and sodium carbonates.

$2KNaC_4H_4O_6$ becomes $Na_2CO_3 + K_2CO_3$.

$2KNaC_4H_4O_64H_2O = 2H_2SO_4 = 4H$.

564 grammes = 4 grammes.

141 ,, = 1 gramme = 1,000 c.c. N. sol.

0·0141 gramme = 1 c.c. N/10 ,,

Weigh out about 1·4 grammes of the sample, incinerate and titrate as directed for potassium citrate.

Sodium Benzoate.—This salt when heated to redness is converted into sodium carbonate.

$2C_6H_5COONa$ becomes Na_2CO_3.

$2C_6H_5COONa = H_2SO_4 = 2H$.

288 grammes = 2 grammes.

144 ,, = 1 gramme = 1,000 c.c. N. solution.

0·0144 gramme = 1 c.c. N/10 ,,

Weigh out about 1·4 grammes and proceed as directed for potassium citrate. Not less than 96 per cent. of the pure salt should be present.

Sodium Salicylate.—The purity of this salt is determined in the same way as for sodium benzoate.

$2C_6H_4OHCOONa$ becomes Na_2CO_3.

$2C_6H_4OHCOONa = H_2SO_4 = 2H$.

320 grammes = 2 grammes.

160 ,, = 1 gramme = 1,000 c.c. N. sol.

0·016 gramme = 1 c.c. N/10 ,,

Weigh out about 1·6 grammes and proceed as directed for potassium citrate.

It should contain at least 99·5 per cent. of the pure salt.

Potassium Acetate.—This salt is converted by ignition into potassium carbonate, and the purity is determined in the same way as for potassium citrate.

$2CH_3COOK$ becomes K_2CO_3.

$2CH_3COOK = H_2SO_4 = 2H.$

196 grammes = 2 grammes.

98 ,, = 1 gramme = 1,000 c.c. N. solution.

0·0098 gramme = 1 c.c. N/10 ,,

Take about 1 gramme and proceed as directed for potassium citrate. At least 90 per cent. of the pure salt should be present.

Ammoniated Mercury.—This substance has the composition NH_2HgCl, and when treated with a solution of potassium iodide yields mercuric iodide, ammonia and potassium hydroxide according to the equation

$$NH_2HgCl + 2KI + H_2O = HgI_2 + NH_3 + KOH + KCl.$$

If an excess of potassium iodide is used the mercuric iodide dissolves and a clear solution is obtained. This reaction is quantitative and is made use of in determining the purity of the substance. A weighed quantity is decomposed with excess of potassium iodide, and the alkalis produced are titrated with standard acid.

From the above equation

$NH_2HgCl = NH_3 + KOH = 2H.$

252 grammes = 2 grammes.

126 ,, = 1 gramme = 1,000 c.c. N. sol.

0·0126 gramme = 1 c.c. N/10 ,,

Weigh out 0·3 gramme of the sample and triturate in a mortar with a little water, transfer to a flask by means of 40 c.c. of water, then rinse the mortar with 10 c.c. of a 20 per cent. potassium iodide solution, pouring the solution into the flask ; stopper the flask and shake gently until a clear solution is obtained. Titrate with N/10 hydrochloric or sulphuric acid, using methyl orange as indicator. Not less than 94·5 per cent. of the pure substance should be present.

CHAPTER V

ACIDIMETRY AND ALKALIMETRY (*continued*)

Determinations with Sodium Hydroxide and Barium Hydroxide.

Normal Sodium Hydroxide Solution.

The equation

$$NaOH + HCl = NaCl + H_2O$$

shows that the normal solution of sodium hydroxide contains the gramme-molecular weight (40 grammes) in 1,000 c.c.

Sodium hydroxide is never quite pure, as it absorbs moisture and carbon dioxide from the air, and an accurate volumetric solution cannot be made by simply dissolving up the correct weight of the solid substance. An approximately normal solution is prepared and then standardised with N. sulphuric acid. Owing to the presence of small quantities of carbonate the volume of N. acid required by a given volume is different according as methyl orange or phenol-phthalein is used as indicator (*see* p. 20). Two factors are therefore required, and the solution must be standardised for both indicators.

Weigh out about 42 grammes of sodium hydroxide

and dissolve in about 700 c.c. of water. Cool the solution thoroughly and dilute to 1,000 c.c. Measure out 20 c.c. and titrate with N. sulphuric acid, using methyl orange as indicator. Repeat, using phenol-phthalein as indicator, and calculate the two factors in the usual way.

The solution should be kept in a bottle closed with a rubber stopper, as it attacks glass and causes a glass stopper to stick.

The standardisation should be repeated at intervals as the solution takes up carbon dioxide from the air.

Standard solution of sodium hydroxide is used for the determination of a large number of acids. For practice the student should make the following determinations.

Oxalic Acid.

The reaction between oxalic acid and sodium hydroxide is expressed by the equation

$$H_2C_2O_4 + 2NaOH = Na_2C_2O_4 + 2H_2O.$$

$$H_2C_2O_4.2H_2O = 2NaOH = 2H.$$

$$\begin{array}{lll} 126 \text{ grammes} & = 2 \text{ grammes.} & \\ 63 \quad ,, & = 1 \text{ gramme} & = 1{,}000 \text{ c.c. N. sol.} \\ 0{\cdot}0063 \text{ gramme} & & = 1 \text{ c.c. N/10} \quad ,, \end{array}$$

Weigh out about 0·7 gramme of oxalic acid crystals and dissolve in sufficient water to produce 100 c.c. Titrate 20 c.c. of N/10 sodium hydroxide solution with the oxalic acid solution, using phenol-phthalein as indicator. Calculate the purity of the acid.

Sodium Hydrogen Sulphate.

Acid salts may also be determined by titration with a standard solution of alkali. The reaction in the case of sodium hydrogen sulphate is expressed by the equation

$NaHSO_4 + NaOH = Na_2SO_4 + H_2O.$

$NaHSO_4 = NaOH = H.$

120 grammes $=$ 1 gramme $=$ 1,000 c.c. N. sol.

0·012 gramme $=$ 1 c.c. N/10 ,,

Weigh out about 1·2 grammes of the salt, dissolve in water and dilute to 100 c.c. Titrate 20 c.c. of N/10 sodium hydroxide solution with the acid solution, using methyl orange as indicator. Calculate the purity of the salt.

Sodium hydrogen oxalate, potassium hydrogen sulphate, and other salts of the same type may be determined in the same way.

Phosphoric Acid and Phosphates.

Phosphoric acid, H_3PO_4, is a tribasic acid and forms three series of salts according as one, two or all of the hydrogen atoms are replaced by metals. The salts differ in their reactions towards various indicators and simple methods of determination are based upon these differences. The behaviour of aqueous solutions of phosphoric acid and its sodium salts is shown in the table on page 34.

Concentrated Phosphoric Acid.

From the table, it is apparent that when a solution of phosphoric acid is titrated with standard sodium

	Methyl Orange.	Phenol-phthalein.	Litmus.
Phosphoric acid, H_3PO_4 .	Acid	Acid	Acid
Sodium dihydrogen phosphate, NaH_2PO_4 . .	Neutral	Acid	Acid
Disodium hydrogen phosphate, Na_2HPO_4	Alkaline	Neutral	Neutral
Trisodium phosphate, Na_3PO_4 .	Alkaline	Alkaline	Alkaline

hydroxide solution, using methyl orange as indicator, the solution becomes yellow when all the acid has been changed into sodium dihydrogen phosphate according to the equation

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O.$$

On adding phenol-phthalein and continuing the titration the solution does not turn pink until all the phosphoric acid has been converted into disodium hydrogen phosphate, thus :—

$$NaH_2PO_4 + NaOH = Na_2HPO_4 + H_2O.$$

The end-reaction with phenol-phthalein is made sharper by the addition of sodium chloride.

The quantity of alkali solution required in each stage of the titration is the same, and the amount of phosphoric acid may be calculated from either reading, thus :—

$H_3PO_4 = NaOH = H.$

98 grammes = 1 gramme = 1,000 c.c. N. sol.

0·098 gramme = 1 c.c. ,, ,,

Weigh out about 10 grammes of the sample and dilute

to 100 c.c. Take 20 c.c., add methyl orange and titrate with N. sodium hydroxide solution. When the end-point is reached, read the burette, add phenol-phthalein and 10 grammes of sodium chloride dissolved in 40 c.c. of water, and again titrate with N. sodium hydroxide solution.

For pharmaceutical purposes concentrated phosphoric acid should contain 66·3 per cent. of hydrogen phosphate.

Acid Sodium Phosphate.

The purity of sodium dihydrogen phosphate,

$$NaH_2PO_4,$$

is determined by titration with standard sodium hydroxide solution, using phenol-phthalein as indicator. From the table on p. 34 it is evident that the alkaline reaction will be produced when all the salt has been converted into disodium hydrogen phosphate, according to the equation

$$NaH_2PO_4 + NaOH = Na_2HPO_4 + H_2O.$$

The end-reaction is not quite sharp in aqueous solution, but the colour change is easily seen if the solution contains 50 per cent. of glycerine.

From the above equation

$$NaH_2PO_4 = NaOH = H.$$

120 grammes = 1 gramme = 1,000 c.c. N. sol.

0·12 gramme = 1 c.c. ,, ,,

Weigh out about 10 grammes and dissolve it in sufficient water to produce 100 c.c. Take 20 c.c., add an equal volume of glycerine and titrate with N. sodium hydroxide solution, using phenol-phthalein as indicator.

For pharmaceutical purposes at least 70 per cent. of the pure salt, NaH_2PO_4, should be present.

Sodium Phosphate.

The purity of disodium hydrogen phosphate,

$$Na_2HPO_4.12H_2O,$$

is determined by titration with standard sulphuric acid, using methyl orange as indicator. The table on page 34 shows that this indicator will give a red colour when all the salt has been changed into sodium dihydrogen phosphate, thus

$2Na_2HPO_4 + H_2SO_4 = 2NaH_2PO_4 + Na_2SO_4.$
$2Na_2HPO_4.12H_2O = H_2SO_4 = 2H.$
716 grammes = 2 grammes.
358 „ = 1 grm. = 1,000 c.c. N. sol.
0·358 gramme = 1 c.c. „ „

Take 5 grammes of the sample, dissolve in about 50 c.c. of water and titrate with N. sulphuric acid, using methyl orange as indicator.

For pharmaceutical purposes at least 99·5 per cent. of the hydrate, $Na_2HPO_4.12H_2O$, should be present.

Boric Acid.

The acid properties of this substance are very feeble, and in aqueous solution it cannot be titrated with the ordinary indicators. As already mentioned, it has no action on methyl orange, and although it affects phenolphthalein, if the titration is attempted in aqueous solution with sodium hydroxide solution the pink colour appears before all the acid is neutralised. If, however, glycerine is added in sufficient quantity to form 30 per cent. of the final volume of the reacting mixture the end-reaction is shown when all the boric acid has been converted into sodium metaborate according to the equation

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O.$$

The manner in which the glycerine acts is not definitely known, but a possible explanation is that it combines with the boric acid to form a monobasic glyceryl-boric acid which is a sufficiently strong acid to give a sharp end-point with phenol-phthalein.

From the above equation

$H_3BO_3 = NaOH = H.$

62 grammes $=$ 1 gramme $=$ 1,000 c.c. N. sol.

0·062 gramme $=$ 1 c.c. „ „

Weigh out 1 gramme of boric acid, dissolve in 25 c.c. of water, add at least 20 c.c. of glycerine and titrate with N. sodium hydroxide solution, using phenol-phthalein as indicator.

The glycerine must be free from acidity.

For pharmaceutical purposes not less than 99·5 per cent. of pure acid should be present.

Standard Barium Hydroxide Solution.

A standard solution of barium hydroxide is a valuable acidimetric reagent in certain cases. It is especially useful for the titration of weak organic acids, sharp end-reactions being secured by the use of phenol-phthalein as indicator. A deci-normal solution is the most convenient strength.

From the equation

$Ba(OH)_2 + 2HCl = BaCl_2 + 2H_2O$

$Ba(OH)_2.8H_2O = 2H.$

315·5 grammes $=$ 2 grammes.

157·75 „ $=$ 1 gramme $=$ 1,000 c.c. N. sol.

15·775 „ $=$ 1,000 c.c. N/10 „

Weigh out about 18 grammes of crystallised barium hydroxide and dissolve in sufficient freshly boiled and

cooled distilled water to make 1,000 c.c. Filter quickly if necessary. Titrate 20 c.c. of N/10 sulphuric acid (or preferably hydrochloric acid) with the solution, using phenol-phthalein as indicator, and adjust the strength by dilution or calculate a factor as already described. The solution very readily reacts with carbon dioxide precipitating barium carbonate, and its accuracy can be maintained only by the complete exclusion of carbon dioxide. The water used for the preparation or dilution of the solution must be recently boiled and cooled and the air in contact with the solution must be freed from carbon dioxide. The solution should be preserved in a bottle fitted with an india-rubber stopper and soda-lime tube, and the burette from which the solution is delivered should be stoppered in the same way, so that the air entering is freed from carbon dioxide. Even with these precautions it is advisable to re-standardise the solution each time before use.

Benzoic and Salicylic Acids.

The purity of these acids may be determined by direct titration with N/10 barium hydroxide solution.

From the equations

$$Ba(OH)_2 + 2C_6H_5COOH = (C_6H_5COO)_2Ba + 2H_2O$$

$$Ba(OH)_2 + 2C_6H_4(OH)COOH = (C_6H_4OHCOO)_2Ba + 2H_2O$$

C_6H_5COOH or $C_6H_4(OH)COOH = H.$

122 grammes 138 grammes = 1 gramme.

·0122 gramme ·0138 gramme = 1 c.c. N/10 sol.

Weigh out about 0·5 gramme of the acid and dissolve in a mixture of alcohol and water, add phenol-phthalein and titrate with N/10 barium hydroxide solution. The

alcohol used must first be made neutral to phenol-phthalein.

Ammonium Benzoate and Salicylate.

The purity of these salts may be determined by liberating the acid by means of sulphuric acid, separating it in the free state by shaking out with chloroform and titrating it with N/10 barium hydroxide solution.

$C_6H_5COONH_4$ or $C_6H_4OHCOONH_4 = H$.

·139 grammes	155 grammes	= 1 gramme.
·0139 gramme	·0155 gramme	= 1 c.c. N/10 sol.

Weigh out about 0·5 gramme of the salt, dissolve it in 10 c.c. of water in a separating funnel and add 5 c.c. of diluted sulphuric acid. Add 25 c.c. of chloroform and shake thoroughly. Allow the two liquids to separate completely and draw off the chloroform layer. Repeat the extraction with 15 c.c. and again with 10 c.c. of chloroform. Mix and filter the chloroform solutions and allow the solvent to evaporate at laboratory temperature to about 5 c.c. Then add neutralised alcohol and water and titrate with N/10 barium hydroxide solution, using phenol-phthalein as indicator.

Borax.—The method described for the determination of boric acid may be used for borax also. As shown on page 24, when sulphuric acid is added to a solution of borax in sufficient quantity to make the liquid neutral to methyl orange, all the boric acid originally combined in the borax is set free, and may be titrated with standard solution of sodium hydroxide.

From the equations already given

$Na_2B_4O_7 10H_2O = 4H_3BO_3 = 4NaOH = 4H$.

382 grammes	= 4 grammes.
95·5 ,,	= 1 gramme = 1,000 c.c. N. solution.
0·00955 gramme	= 1 c.c. N/10 solution.

To the solution obtained by titrating the borax with sulphuric acid

(*see* p. 24) add an equal volume of glycerine and titrate with N/10 sodium hydroxide solution, using phenol-phthalein as indicator.

The student should note that 1 c.c. of N/10 acid requires twice as much borax as 1 c.c. of N/10 alkali.

Acetic Acid.—The acid of the British Pharmacopœia should contain 33 per cent. of hydrogen acetate, CH_3COOH.

The strength is determined by titration with standard sodium hydroxide solution. The acid should be weighed in a stoppered bottle to avoid loss by volatilisation. The following equation represents the reaction.

$$CH_3COOH + NaOH = CH_3COONa + H_2O,$$

whence $CH_3COOH = H.$

60 grammes = 1 gramme = 1,000 c.c. N. sol.

0·006 gramme = 1 c.c. N/10 „

Weigh out about 2 grammes of the acid and dilute to 100 c.c. Take 20 c.c. of N/10 sodium hydroxide solution and titrate with the acid solution, using phenol-phthalein as indicator.

Diluted Acetic Acid should contain 5 per cent. of hydrogen acetate. Weigh out about 14 grammes and proceed as for acetic acid.

Glacial Acetic Acid should contain not less than 98·9 per cent. of hydrogen acetate.

Weigh out 0·7 gramme and proceed as for acetic acid.

Acetum Scillae and Acetum Urgineae.—These preparations should contain 6·06 per cent. of acetic acid.

Weigh out about 12 grammes and proceed as for acetic acid.

Oxymel should contain at least 3·84 per cent. of acetic acid. The yellow colour of this preparation may make the end-point with phenol-phthalein difficult to determine. The best procedure is to place a weighed quantity in the titrating flask, dilute well with water and run in the standard sodium hydroxide solution from the burette. Take 25 grammes, dilute well and titrate with N/2 sodium hydroxide solution, using phenol-phthalein as indicator.

Oxymel Scillae and Oxymel Urgineae.—These preparations should contain at least 1·43 per cent. of acetic acid. Weigh out 25 grammes and proceed as for oxymel.

Hydrochloric Acid.—The hydrochloric acid of the British Pharmacopœia should contain 31·79 per cent. of hydrogen chloride. The strength of the acid is determined by titration with standard sodium hydroxide solution. The acid must also be titrated with standard silver nitrate solution, as described on p. 105, in order to make sure that other acids are absent.

The neutralisation with sodium hydroxide is expressed by the equation

$$HCl + NaOH = NaCl + H_2O,$$

whence $HCl = H$.

36·5 grammes = 1 gramme = 1,000 c.c. N. solution.

0·0365 gramme = 1 c.c. ,, ,,

Weigh out 10 grammes of the acid and dilute to 100 c.c. Titrate 20 c.c. of N. sodium hydroxide solution with the diluted acid, using methyl orange as indicator.

Diluted Hydrochloric Acid should contain 10 per cent. of hydrogen chloride.

Weigh out about 4 grammes of the sample and proceed as for the concentrated acid, using N/10 instead of N. sodium hydroxide solution.

Diluted Hydrobromic Acid.—The hydrobromic acid of the British Pharmacopœia should contain 10 per cent. of hydrogen bromide. The strength is determined by means of standard sodium hydroxide solution, and the result must be checked by a titration with standard silver nitrate solution as for hydrochloric acid.

The following equation represents the reaction with sodium hydroxide :—

$$HBr + NaOH = NaBr + H_2O,$$

whence $HBr = H$.

81 grammes = 1 gramme = 1,000 c.c. N. solution.

0·0081 gramme = 1 c.c. N/10 ,,

Weigh out 10 grammes of the sample and dilute to 100 c.c. Titrate 20 c.c. of N/10 sodium hydroxide solution with the diluted acid, using methyl orange as indicator.

Nitric Acid.—The nitric acid of the British Pharmacopœia should contain 70 per cent. of hydrogen nitrate.

The neutralisation with sodium hydroxide is expressed by the equation

$$HNO_3 + NaOH = NaNO_3 + H_2O,$$

whence $HNO_3 = H$.

63 grammes = 1 gramme = 1,000 c.c. N. solution.

0·063 gramme = 1 c.c. ,, ,,

Weigh out about 10 grammes of the sample and dilute to 100 c.c. Titrate 20 c.c. of N. sodium hydroxide solution with the diluted acid, using methyl orange as indicator.

Diluted Nitric Acid should contain 10 per cent. of hydrogen nitrate.

Weigh out about 4 grammes and proceed as for nitric acid, using N/10 instead of N. sodium hydroxide solution.

Diluted Nitro-hydrochloric Acid.—This acid is an aqueous solution of hydrochloric, nitric and nitrous acids, with some free chlorine.

10 c.c. should require for neutralisation about 26·6 c.c. of N. sodium hydroxide solution. Methyl orange is a suitable indicator.

Sulphuric Acid.—The sulphuric acid of the British Pharmacopœia should contain not less than 95 per cent. of hydrogen sulphate.

From the equation given on p. 7, 0·049 gramme of H_2SO_4 is contained in 1 c.c. of N. solution.

Weigh out about 5 grammes of the acid, add to it about 60 c.c. of water, cool and make up to 100 c.c. Titrate 20 c.c. of N. sodium hydroxide with the diluted acid, using methyl orange or phenol-phthalein as indicator.

Diluted Sulphuric Acid should contain 10 per cent. of hydrogen sulphate.

Weigh out about 5 grammes and proceed as for sulphuric acid, using N/10 instead of N. sodium hydroxide solution.

Aromatic Sulphuric Acid.—This preparation consists of a solution of sulphuric acid in alcohol containing aromatic ingredients. Some of the acid exists as ethyl hydrogen sulphate, $C_2H_5HSO_4$, but when diluted with water the liquid behaves towards alkalis as though all the acid were free. The ethyl hydrogen sulphate is decomposed by water thus :—

$$C_2H_5HSO_4 + H_2O = C_2H_5OH + H_2SO_4.$$

The neutralising power should be equal to that of a 13·2 per cent. solution of hydrogen sulphate. Old samples may become very dark in colour, and the solution to be titrated should be well diluted with water or the end-point may be obscured.

Weigh out about 5 grammes of the sample and dilute to 100 c.c. Take 20 c.c. of N/10 sodium hydroxide solution, dilute freely, and titrate with the diluted acid, using phenol-phthalein as indicator.

Diluted Phosphoric Acid should contain 10 per cent. of hydrogen phosphate. The strength is determined in the same way as the concentrated acid. Ten grammes should be taken for each titration.

Lactic Acid.—The lactic acid of the British Pharmacopœia should contain at least 75 per cent. of hydrogen lactate, $CH_3CHOHCOOH$, and 10 per cent. of lactide, $C_6H_8O_4$. The lactic acid is determined by neutralisation with sodium hydroxide in accordance with the equation $HC_3H_5O_3 + NaOH = NaC_3H_5O_3 + H_2O$,

whence $HC_3H_5O_3 = H$.

90 grammes = 1 gramme = 1,000 c.c. N. solution.

0·09 gramme = 1 c.c. „ „

Weigh out about 10 grammes of the acid and dilute to 100 c.c. Titrate 20 c.c. of the diluted acid with N. sodium hydroxide solution. Phenol-phthalein or litmus may be used as indicator.

The determination of lactide is described on p. 53.

Citric Acid.—Crystalline citric acid should contain at least 99·5 per cent. of the hydrate $H_3C_6H_5O_7.H_2O$. It is a tribasic acid and the reaction with sodium hydroxide is represented by the equation

$$H_3C_6H_5O_7 + 3NaOH = Na_3C_6H_5O_7 + 3H_2O,$$

$H_3C_6H_5O_7.H_2O = 3NaOH = 3H.$
210 grammes = 3 grammes.
70 ,, = 1 gramme = 1,000 c.c. N. solution.
0·007 gramme = 1 c.c. N/10 ,,

Weigh out about 1 gramme of the sample, dissolve in water, and dilute to 100 c.c. Take 20 c.c. of N/10 sodium hydroxide solution and titrate with the acid solution, using phenol-phthalein as indicator.

Lemon Juice is required to contain between 7 and 9 grammes of citric acid in 100 c.c.

Take 10 c.c. of the sample and dilute to 100 c.c. Titrate as directed for citric acid.

Tartaric Acid.—The neutralisation of tartaric acid by sodium hydroxide is expressed by the equation

$$H_2C_4H_4O_6 + 2NaOH = Na_2C_4H_4O_6 + 2H_2O,$$

whence $H_2C_4H_4O_6 = 2NaOH = 2H.$
150 grammes = 2 grammes.
75 ,, = 1 gramme = 1,000 c.c. N. sol.
0·0075 gramme = 1 c.c. N/10 ,,

Weigh out 1 gramme of the sample and dissolve in sufficient water to make 100 c.c. Titrate 20 c.c. of N/10 sodium hydroxide with the acid solution. Phenol-phthalein or litmus may be used as indicator. Not less than 99 per cent. of pure acid should be present.

Acid Potassium Tartrate.—The purity of this salt may be determined by titration with standard sodium hydroxide solution. The disadvantage of this method is referred to on p. 28. As the salt is only slightly soluble in cold water the solution must be kept boiling during the titration.

From the equation

$$KHC_4H_4O_6 + NaOH = KNaC_4H_4O_6 + H_2O,$$

$KHC_4H_4O_6 = NaOH = H.$
188 grammes = 1 gramme = 1,000 c.c. N. solution
0·188 gramme = 1 c.c. ,, ,,

Weigh out 1 gramme of the salt into the titrating flask, add water

and phenol-phthalein. Heat to boiling and run in N/2 solution of sodium hydroxide until a permanent pink colour is obtained.*

Titration of Carbonates and Bicarbonates with Organic Acids.—The British Pharmacopœia gives figures for the amounts of tartaric acid, citric acid and lemon juice, which should neutralise definite quantities of alkali carbonates and bicarbonates. In checking these figures for any particular pair of samples, the indicator to be used is phenol-phthalein, and the liquid must be boiled to expel the carbon diox de liberated.

For practice find the weight of tartaric acid required to neutralise 20 grammes of sodium bicarbonate.

The reaction taking place is expressed thus :—

$$H_2C_4H_4O_6 + 2NaHCO_3 = Na_2C_4H_4O_6 + 2H_2O + 2CO_2.$$

Prepare solutions of each substance containing 1 gramme in 100 c.c. Place 20 c.c. of the bicarbonate solution in the titrating flask, dilute, bring to the boil, and titrate with the acid solution until the pink colour no longer returns on boiling.

Picric Acid.—This substance is a trinitrophenol, but in its behaviour towards alkalis it resembles the weaker acids, so that it may be titrated with a standard solution of an alkali. Difficulties arise in the determination of picric acid from its comparatively small solubility in cold water and from the deep yellow colour of even dilute solutions. If the solution of the acid is run into the solution of alkali tinted with phenol-phthalein, the liquid at first has a deep orange colour, and the change from this to the yellow of sodium picrate is not easily seen. The titration should be carried out by dissolving a weighed quantity in hot water and running in the standard alkali from a burette, using phenol-phthalein as indicator. If the alkali is of normal or seminormal strength the change from yellow to red is well marked on the addition of one drop more than the quantity of solution necessary to neutralise.

From the equation

$$C_6H_2(NO_2)_3OH + NaOH = C_6H_2(NO_2)_3ONa + H_2O,$$
$$C_6H_2(NO_2)_3OH = NaOH = H.$$
$$229 \text{ grammes} = 1 \text{ gramme} = 1{,}000 \text{ c.c. N. sol.}$$
$$0{\cdot}1145 \text{ gramme} = 1 \text{ c.c. N/2 ,,}$$

Take 2 grammes, dissolve in hot water and titrate with N/2 sodium hydroxide solution, using phenol-phthalein as indicator.

It should contain at least 99 per cent. of the pure trinitrophenol.

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* The carbon dioxide evolved from the carbonate present is expelled during the boiling and the methyl orange factor must be used.

Acidity of Solution of Hydrogen Peroxide.—Commercial solutions of hydrogen peroxide usually contain small quantities of acid, purposely retained to prevent decomposition, the peroxide being unstable in presence of alkali. An excessive amount of acid would render the solution unsuitable for some of the purposes for which it is used, and the amount present therefore must be known.

Take 20 c.c. and titrate with N/10 sodium hydroxide solution, using methyl orange as indicator.

Phenol-phthalein may not be used as indicator because the results obtained are greater than when methyl orange is used. If phosphoric acid is present, as is frequently the case, the reason for this is apparent from the considerations mentioned on p. 34.

100 c.c. should not contain more than 0·098 gramme of acid calculated as phosphoric acid.

CHAPTER VI

ACIDIMETRY AND ALKALIMETRY (*continued*)

Residual or " Back " Titration.

In describing the determination of ammonia on p. 20, it was mentioned that the method of direct titration may give erroneous results owing to volatilisation of ammonia during the titration. A correct result may be obtained by the following method. The solution is measured out and immediately mixed with a measured volume of standard acid which is more than sufficient to neutralise it. The volatile ammonia is thus converted into a non-volatile salt. The excess of acid is then found by titration with standard alkali solution, and the quantity of acid necessary to neutralise the ammonia is obtained by difference.

Methods such as this, in which an excess of the standard reagent is used and the excess determined after completion of the reaction, are referred to as residual or back titrations. There are many determinations in which back titration is advantageous and many in which it is the only possible method. It is commonly used :—

(*a*) where the solution under test may alter in strength

during a direct titration by reason of volatilisation, *e.g.* solution of ammonia ;

(*b*) where the result of a direct titration is vitiated by the occurrence of some unavoidable chemical change, *e.g.* the oxidation of sodium sulphite referred to on p. 99 ;

(*c*) where the substance under test is only slightly soluble in water. A direct titration in many of these cases can be carried out with the substance in suspension, but the back titration is usually more rapid and accurate, *e.g.* lithium carbonate ;

(*d*) where the reaction takes place slowly or requires special conditions to make it complete, *e.g.* lactide and hexamine.

The use of normal solutions for these determinations simplifies the calculations.

Ammonia.

Weigh out about 10 grammes of the ammonia solution, and add it to 50 c.c. of N. sulphuric acid, add methyl orange and titrate with N. sodium carbonate solution. Since equal volumes of normal solutions are equivalent to one another, the reading of sodium carbonate solution, subtracted from 50 c.c., gives the volume of N. sulphuric acid neutralised by the ammonia in the quantity of solution taken.

Ammonium Salts.

The decomposition of ammonium salts by means of sodium hydroxide, with evolution of ammonia, may be employed for their determination. A known volume of standard alkali solution, in excess of that required to decompose all the ammonium salt, is added, the

ammonia is expelled by boiling, and the excess of sodium hydroxide is then found by titration with standard acid.

For practice, determine the purity of ammonium sulphate.

The reaction is represented by the equation

$$(NH_4)_2SO_4 + 2NaOH = 2NH_3 + Na_2SO_4 + 2H_2O,$$

$$(NH_4)_2SO_4 = 2NaOH = 2H.$$

132 grammes = 2 grammes.

66 ,, = 1 gramme = 1,000 c.c. N. sol.

0·066 gramme = 1 c.c. ,, ,,

Weigh out 2 grammes of ammonium sulphate crystals, dissolve in water, and dilute to 100 c.c. Take 20 c.c., add 20 c.c. of N. sodium hydroxide solution, and boil until a piece of litmus paper held in the steam no longer shows an alkaline reaction. Titrate with N. sulphuric acid, using methyl orange as indicator. The reading of sulphuric acid subtracted from 20 c.c. gives the volume of N. sodium hydroxide solution necessary to decompose the ammonium sulphate.

This method cannot be applied when any other substance which reacts with sodium hydroxide is present, as in the determination of ammonia in certain double salts. For example, if the titration of ferrous ammonium sulphate by this method is attempted, the sodium hydroxide precipitates ferrous hydroxide and the titration with acid is not possible.

A method of more general application is to decompose the salt with concentrated solution of alkali and collect the ammonia evolved in a known volume of standard acid and to determine the excess of acid with standard alkali.

The apparatus required is shown in Fig. 1. The 600 c.c. flask A contains the ammonium salt and a little water. A strong solution of sodium hydroxide is added from the tap-funnel B. The ammonia passes in the

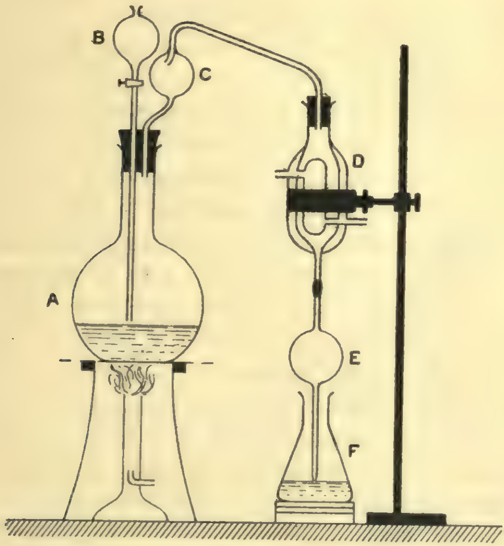

FIG. 1.

steam through the splash-bulb C and the small double-surface condenser D into the standard acid, contained in the 300 c.c. receiving flask F. The splash-bulb C is used to prevent the fine spray of alkaline solution, which is always given off by boiling solutions of sodium hydroxide, from passing over into the acid. The bulb E prevents the acid from passing over into A when the

liquid is cooled by the addition of more sodium hydroxide solution. The point of the delivery tube should dip just below the surface of the acid in F, and the flask should be supported at the commencement on a number of wooden blocks which can be removed one by one as the liquid accumulates. A little porous pot should be placed in the flask A, to prevent bumping.

Weigh out 0·6 gramme of ammonium sulphate and place it in the flask A with 50 c.c. of water. Measure 25 c.c. of N. sulphuric acid into the flask F. Add from B about 20 c.c. of a 20 per cent. solution of sodium hydroxide to the liquid in A and heat until the solution boils gently. Continue the distillation for twenty to thirty minutes, adding more sodium hydroxide solution from B as required. Dilute the acid to 250 c.c. and titrate 20 c.c. of N/10 sodium hydroxide with this solution.

When applying this process to a substance in which the proportion of ammonia is not known, the standard acid in F should be tinted with methyl orange. If the liquid turns yellow, the acid has all been neutralised and more must be added.

Calcium Salts.

The precipitation of calcium as carbonate when sodium carbonate is added to a solution of a calcium salt, may be used for the determination of calcium.

A measured volume of standard sodium carbonate solution, in excess of that required for the complete precipitation of the calcium, is used, the calcium carbonate is filtered off, and the sodium carbonate in the filtrate is determined by means of standard acid.

Find the proportion of anhydrous calcium nitrate in the commercial substance.

The result is calculated from the equation

$Ca(NO_3)_2 + Na_2CO_3 = CaCO_3 + 2NaNO_3.$

$Ca(NO_3)_2 = Na_2CO_3 = 2H.$

164 grammes = 2 grammes.

82 ,, = 1 gramme = 1,000 c.c. N. sol.

0·082 gramme = 1 c.c. ,, ,,

Take about 0·5 gramme of the substance, dissolve in water and add 20 c.c. of N. sodium carbonate solution. Heat to about 70° C., allow to cool, filter and wash the precipitate well. Titrate the mixed filtrate and washings with N. sulphuric acid, using methyl orange as indicator. The reading of acid solution subtracted from 20 c.c. gives the volume of N. sodium carbonate solution required to react completely with 0·5 gramme of the sample.

This method may also be used for the determination of barium and strontium salts.

Aromatic Spirit of Ammonia.—The ammonium carbonate is determined by precipitation with barium chloride, the barium carbonate produced being dissolved in excess of standard hydrochloric acid and the excess titrated back with standard alkali.

The spirit contains true ammonium carbonate, $(NH_4)_2CO_3$, which is formed from ammonium carbamate by the action of water as shown on p. 25, and from ammonium hydrogen carbonate by the action of ammonia thus

$$NH_4HCO_3 + NH_3 = (NH_4)_2CO_3.$$

On adding barium chloride, precipitation takes place according to the equation

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl.$$

The barium carbonate is neutralised according to the equation

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O.$$

From the equations given

$N_3H_{11}C_2O_5\{NH_4HCO_3 + CO(NH_2)(ONH_4)\} = 2(NH_4)_2CO_3$ and

$N_3H_{11}C_2O_5 = 2BaCO_3 = 4H.$

157 grammes = 4 grammes.

39·25 ,, = 1 gramme = 1,000 c.c. N. sol.

·03925 gramme = 1 c.c. ,, ,,

Take 20 c.c., add 50 c.c. of water and excess of a 10 per cent. barium chloride solution and heat the mixture to 70° C. Filter and wash the precipitate until the washings are no longer alkaline. Dissolve the precipitate in 20 c.c. of N/1 hydrochloric acid, heat to boiling, cool and titrate back with N/1 sodium hydroxide solution.

100 c.c. should contain between 2·35 and 2·51 grammes of ammonium hydrogen carbonate and ammonium carbamate calculated together as $N_3H_{11}C_2O_5$.

Carbonates and Oxides.—The process of back titration may be used for the determination of those carbonates and oxides which are insoluble or only slightly soluble in water, such as lithium carbonate or the carbonates and oxides of magnesium and zinc. Although it is possible in some cases to suspend the substance in water and titrate with a standard acid, more accurate results are obtained by dissolving it in an excess of the acid and titrating back with standard alkali solution.

For practice the student should make the following determinations :—

Lithium Carbonate.—Dissolve 1 gramme in 50 c.c. of N. sulphuric acid and titrate the excess of sulphuric acid with N. sodium hydroxide solution, using methyl orange as indicator. The result is calculated from the equation given on p. 27.

Lithium Citrate.—The purity is determined by the method given for potassium citrate. Lithium carbonate is produced on incineration, and owing to its slight solubility in water is best titrated by the residual method.

$2Li_3C_6H_5O_7.4H_2O$ yield $3Li_2CO_3$,

$2Li_3C_6H_5O_74H_2O = 3H_2SO_4 = 6H.$

2 × 282 grammes = 6 grammes.

94 ,, = 1 gramme = 1,000 c.c. N. sol

0·094 gramme = 1 c.c. ,, ,,

Weigh out 3 grammes of the sample and heat in a crucible until completely charred. Extract the residue by warming with

50 c.c. of N. sulphuric acid, filter into a 100-c.c. flask, wash the residue well with hot water and make up the mixed filtrate and washings, after cooling to laboratory temperature, to 100 c.c. Titrate 10 c.c. of the solution with N/10 sodium hydroxide solution, using methyl orange as indicator. One-tenth of the reading of N/10 alkali deducted from 5 c.c. gives the volume of N. sulphuric acid equivalent to 0·3 gramme of the sample. The official salt is required to contain at least 98·5 per cent. of the pure hydrate $Li_3C_6H_5O_7.4H_2O$.

Zinc Oxide.—The calculation will be made from the equation

$ZnO + H_2SO_4 = ZnSO_4 + H_2O.$

$ZnO = H_2SO_4 = 2H.$

81·5 grammes = 2 grammes.

40·75 ,, = 1 gramme = 1,000 c.c. N. solution.

0·004075 gramme = 1 c.c. N/10 ,,

Weigh out about 1·5 grammes of the sample, dissolve it with the aid of gentle heat in 50 c.c. of N. sulphuric acid and titrate the excess of sulphuric acid with N. sodium hydroxide solution, using methyl orange as indicator.

Lactide in Lactic Acid.—Lactide,

$$\begin{array}{ccc} CH_3CH & — & CO \\ | & & | \\ O & & O \\ | & & | \\ OC & — & CH.CH_3 \end{array}$$

is an anhydride of lactic acid and is converted quantitatively into sodium lactate by boiling with sodium hydroxide solution.

The proportion of lactide in the acid, therefore, may be determined by adding excess of standard sodium hydroxide solution; boiling, and titrating back with standard acid.

From the equation

$C_6H_8O_4 + 2NaOH = 2NaC_3H_5O_3.$

$C_6H_8O_4 = 2NaOH = 2H.$

144 grammes = 2 grammes.

72 ,, = 1 gramme = 1,000 c.c. N. solution.

0·072 gramme = 1 c.c. ,, ,,

To the liquid in the flask after titration of the acid (*see* p. 42) add a further 20 c.c. of N. sodium hydroxide solution, boil for 15 minutes and titrate back with N. sulphuric acid.

Chloral Hydrate.—Sodium hydroxide decomposes chloral hydrate with production of chloroform and sodium formate according to the equation.

$CCl_3CH(OH)_2 + NaOH = CHCl_3 + HCOONa + H_2O.$

This reaction is employed for the determination of chloral hydrate. An excess of standard sodium hydroxide solution is added, and after the chloroform has separated, the excess is titrated back with standard acid.

From the above equation

$CCl_3CH(OH)_2 = NaOH = H.$

165·5 grammes = 1 gramme = 1,000 c.c. N. solution.

0·1655 gramme = 1 c.c. „ „

Dissolve about 3 grammes of the sample in 50 to 100 c.c. of water, add 30 c.c. of N. sodium hydroxide solution, and shake for two minutes. Titrate back with N. sulphuric acid, using phenol-phthalein as indicator.

The process is inaccurate because sodium hydroxide decomposes chloroform according to the equation

$$CHCl_3 + 4NaOH = 3NaCl + HCOONa + 2H_2O.$$

If the liquid is shaken too long before titrating back some sodium hydroxide is used up by the chloroform and the result comes out too high.

Good comparative results may be obtained, however, by using the same quantities and employing the same conditions in all experiments.

A more satisfactory method is described on p. 107.

Hexamine.—When hexamine is heated with dilute sulphuric acid, ammonium sulphate is formed and formaldehyde liberated, according to the equation

$$C_6H_{12}N_4 + 2H_2SO_4 + 6H_2O = 2(NH_4)_2SO_4 + 6HCHO.$$

This reaction is employed for the determination of the purity of the drug, which should contain at least 98 per cent. of pure hexamethylenetetramine.

The substance is heated with an excess of standard sulphuric acid, and after all the formaldehyde has been driven off, the excess of acid is titrated with standard alkali solution.

$C_6H_{12}N_4 = 2H_2SO_4 = 2H.$

140 grammes = 2 grammes.

70 „ = 1 gramme = 1,000 c.c. N. solution.

0·07 gramme = 1 c.c. „ „

Take about 5 grammes of the sample and dissolve in sufficient water to make 100 c.c. Take 20 c.c., add 35 c.c. of N. solution of sulphuric acid and heat on the water bath until the liquid no longer smells of formaldehyde, then titrate the excess of acid with N. solution of sodium hydroxide, using methyl orange as indicator.

Solution of Formaldehyde.—Formaldehyde in aqueous solution is readily oxidised to formic acid by various reagents. Thus

$$HCHO + O = HCOOH.$$

The strength of a solution may be found by means of this reaction, either by determining the amount of acid resulting from the oxidation or by performing the reaction with a standard solution of an oxidising agent such as iodine.

The acidimetric determination is best carried out by oxidising the solution with hydrogen peroxide in presence of a known excess of standard alkali solution and titrating back with standard acid.

$$HCOOH + NaOH = HCOONa + H_2O.$$

$HCHO = HCOOH = H.$

30 grammes = 1 gramme = 1,000 c.c. N. solution.

0·03 gramme = 1 c.c. „ „

Mix 3 c.c. of the sample with 50 c.c. of N. sodium hydroxide solution in a 300 c.c. conical flask, add 50 c.c. of hydrogen peroxide solution and heat on the water-bath until the reaction is complete, as shown by the cessation of effervescence. Titrate the excess of sodium hydroxide by means of N. sulphuric acid, using phenol-phthalein as indicator. Solution of hydrogen peroxide usually contains acid, and the error introduced by this must be allowed for.

The usual method is to carry out a duplicate experiment with the reagents, but without the formaldehyde solution, and deduct the volume of sodium hydroxide solution neutralised by the hydrogen peroxide, from the total volume neutralised in the main experiment.

For pharmaceutical purposes the solution should contain between 36 and 38 grammes of formaldehyde in 100 c.c.

The determination by means of iodine is described on p. 99.

CHAPTER VII

DETERMINATIONS INVOLVING OXIDATION AND REDUCTION

A LARGE number of volumetric determinations depend upon the quantitative oxidation of certain substances by titration with a suitable reagent.

Ferrous sulphate, for example, may be converted completely into ferric sulphate by certain oxidising agents in presence of sulphuric acid, thus :—

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

The determination of ferrous salts may be based upon this reaction, if the change is brought about by titration with a solution capable of yielding a known amount of oxygen.

The principal oxidising agents used in volumetric analysis are—potassium permanganate, potassium dichromate, and iodine.

Potassium Permanganate.

In presence of a suitable reducing agent and of sulphuric acid, potassium permanganate acts according to the equation

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

$$\therefore\ 2KMnO_4 = 5O \qquad = 10H.$$

$$316 \text{ grammes} = 80 \text{ grammes} = 10 \text{ grammes}.$$

Two molecules of potassium permanganate thus yield in acid solution five "available" atoms of oxygen.

The term "available oxygen" is applied to the oxygen which is capable of taking part in an oxidising action. Although two molecules of potassium permanganate contain eight atoms of oxygen, it appears from the equation given that only five atoms act upon the reducing substance. This is more readily understood if we consider that the reaction is really a change of the oxide Mn_2O_7, the anhydride of permanganic acid, into MnO, the oxide corresponding to manganous sulphate,

$$Mn_2O_7 = 2MnO + 5O.$$

Three hundred and sixteen grammes of potassium permanganate are therefore equivalent to 80 grammes of oxygen or 10 grammes of hydrogen, and a normal solution will contain 31·6 grammes of potassium permanganate in 1,000 c.c.

A decinormal solution is most commonly employed.

Weigh out 3·16 grammes of the salt, dissolve in water, and dilute to 1,000 c.c.

Potassium permanganate is reduced by any organic matter present in the water, and also undergoes decomposition when the solution is exposed to light. The solution should be stored in a dark place, and should be standardised at frequent intervals by means of ferrous ammonium sulphate or oxalic acid.

Standardisation with Ferrous Ammonium Sulphate.

This salt occurs as pale-green crystals, readily soluble in water and having the composition

$$FeSO_4.(NH_4)_2SO_4.6H_2O.$$

It is more suitable than ferrous sulphate for standardisation purposes as it may be obtained quite pure, and if kept dry remains unchanged for an indefinite period. Combining the equation for the oxidation of ferrous sulphate with that representing the reduction of potassium permanganate, the following equation for the reaction between these two substances is obtained :—

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

$$\therefore\ 10FeSO_4.(NH_4)_2SO_4.6H_2O = 2KMnO_4 = 10H.$$

$$10 \times 392 \text{ grammes} = 10 \text{ grammes}$$

$$\therefore\ 392 \quad \text{,,} \quad = 1 \text{ gramme}$$

$$= 1{,}000 \text{ c.c. N. solution.}$$

Weigh out exactly 3·92 grammes of ferrous ammonium sulphate and dissolve in sufficient water to produce 100 c.c.

The water must first be freed from dissolved air which would oxidise the iron, by boiling for a few minutes and then cooling to room temperature by immersing the flask in cold water. The solution must be prepared just before use, as it is quickly oxidised by the atmosphere.

Take 20 c.c. of the decinormal iron solution thus prepared, add a little dilute sulphuric acid, and titrate with the permanganate solution until a permanent pink colour is produced.

The reduction products of potassium permanganate give a colourless solution, so that while any ferrous salt remains unoxidised the solution remains colourless, but the slightest excess of potassium permanganate produces the characteristic colour and indicates the completion of the oxidation.

Standardisation with Oxalic Acid.

Oxalic acid occurs in colourless crystals having the formula $H_2C_2O_4.2H_2O$. It has the disadvantage that if kept in a dry atmosphere part of the water of crystallisation may be lost. A warm, acidified solution is oxidised by potassium permanganate in accordance with the equation

$$H_2C_2O_4 + O = 2CO_2 + H_2O.$$

Combining this with the equation for the reduction of potassium permanganate (p. 56),

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

$\therefore 5H_2C_2O_4.2H_2O = 2KMnO_4 = 10H.$

5×126 grammes		= 10 grammes.
63	,,	= 1 gramme = 1,000 c.c. N. solution.
0·63 gramme		= 100 c.c. N/10 solution.

Weigh out 0·63 gramme of pure crystallised oxalic acid and dissolve in sufficient water to produce 100 c.c. Take 20 c.c., add dilute sulphuric acid and a considerable amount of water. Heat the solution to about 60° C., and titrate with the potassium permanganate solution until the appearance of a pink colour, which is permanent after warming and shaking, indicates the end of the reaction.

The solution must not be heated too strongly, or a little extra permanganate may be reduced.

The factor of the N/10 potassium permanganate solution is then calculated in the usual way.

The appearance of a brown coloration or precipitate

during the titration indicates a deficiency of sulphuric acid, and more must be added.

Potassium permanganate does not give accurate results when titrating a solution containing much free hydrochloric acid, because the hydrochloric acid reduces potassium permanganate with liberation of chlorine, according to the equation

$$16HCl + 2KMnO_4 = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O.$$

For the determination of iron in presence of hydrochloric acid, potassium dichromate is usually employed, but the titration with potassium permanganate may be made accurate by conducting it slowly with constant shaking, manganous sulphate being added and the liquid being well diluted. The liquid in the flask should contain in each 100 c.c. at least 1 gramme of manganese sulphate and not more than 0·9 gramme of hydrogen chloride.

Purity of Iron Wire.

The purity of a sample of iron may be determined by dissolving a known weight in dilute sulphuric acid and titrating the solution of ferrous sulphate thus obtained with standard potassium permanganate solution. The ferrous salt is liable to oxidation by the air during the process of solution, and it is necessary to prevent access of air by one of the following methods :—

(*a*) The iron is dissolved in a flask supported in an inclined position on a retort stand. The neck is closed by a cork, through which is fitted a long piece of narrow glass tubing. The tube is bent just outside the flask so that the long limb is vertical, and the end is made to dip below the surface of some water contained in a beaker.

The hydrogen evolved by the action of the iron on the acid drives the air from the flask and the water prevents its re-entry (Fig. 2).

(*b*) The flask in which the iron is dissolved may be fitted with a "Bunsen valve," which is made as follows :—

A slit about a $\frac{1}{4}$ inch in length is cut longitudinally in

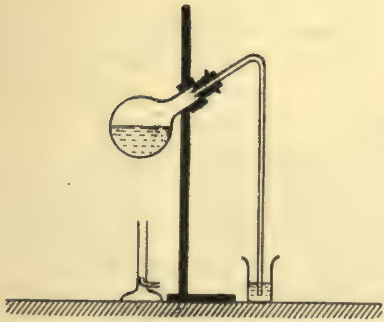

FIG. 2.

FIG. 3.

a piece of narrow rubber tubing about $1\frac{1}{2}$ inches long. One end of the tube is closed with a short piece of glass rod and the other is fitted over a short piece of glass tubing, which passes through the cork of the flask. The slit allows the escape of hydrogen, but prevents entry of the air during cooling. The valve is more effective if the slit is cut from the inside of the rubber tubing (Fig. 3).

Dissolve 0·5 gramme of the sample of wire in dilute sulphuric acid, using one of the methods described above for the prevention of oxidation. Warm the liquid to complete the solution of the iron, cool and make up to 100 c.c. with air-free water. Titrate 20 c.c. with N/10 potassium permanganate solution.

The acid dissolves the iron according to the equation

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

The proportion of pure iron in the sample taken may therefore be calculated from the equivalents

$10Fe = 2KMnO_4 = 10H.$

56 grammes = 1 gramme = 1,000 c.c. N. solution.
·0056 gramme = 1 c.c. N/10 ,,

Iron in Ferric Salts.

The iron in ferric compounds is determined by reduction to the ferrous state and titration of the ferrous salt with standard solution of potassium permanganate. Nascent hydrogen evolved from zinc and sulphuric acid is the most convenient reducing agent.

For practice in the determination, find the proportion of iron in iron ammonium alum

$$Fe_2(SO_4)_3(NH_4)_2SO_4 24H_2O.$$

Dissolve about 5 grammes of the salt in a little water, add zinc (in powder or fine granules and free from iron) and sulphuric acid, and warm gently. Allow the action to proceed until a drop of the liquid when tested on a white tile with potassium thiocyanate solution no longer gives a red colour, showing the absence of ferric iron. Filter and cool the solution, wash out the flask with air-free water, pouring the washings over the filter, and

make up the mixed filtrate and washings to 100 c.c. with air-free water. Titrate 20 c.c. with N/10 potassium permanganate solution.

The iron is reduced according to the equation

$$Fe_2(SO_4)_3 + 2H = 2FeSO_4 + H_2SO_4,$$

and the result is calculated from the equivalents already given, *i.e.*, 0·0056 gramme of iron = 1 c.c. N/10 solution.

Oxalates.

Since oxalates, when treated with sulphuric acid, liberate free oxalic acid, these salts may be determined by titration with standard potassium permanganate in presence of sulphuric acid.

For practice, find the purity of potassium hydrogen oxalate KHC_2O_4.

Dissolve 1·3 grammes of the salt in sufficient water to make 100 c.c. of solution and titrate 20 c.c. with N/10 potassium permanganate solution as described on p. 59.

Oxalic acid is set free according to the equation

$$2KHC_2O_4 + H_2SO_4 = K_2SO_4 + 2H_2C_2O_4,$$

whence

$5KHC_2O_4 = 2KMnO_4 = 10H.$

5 × 128 grammes = 10 grammes.

64 „ = 1 gramme = 1,000 c.c. N. sol.

0·0064 gramme = 1 c.c. N/10 „

Calcium Salts.

The fact that calcium is completely precipitated as oxalate from alkaline solutions may be employed for its determination in the two following ways :—

(*a*) The solution of the salt is treated with a known volume of standard oxalic acid solution, excess of ammonia is added and the liquid heated. The precipi-

tate is filtered off and the excess of oxalic acid determined in the filtrate.

The addition of ammonia is necessary because the oxalate is not precipitated completely in presence of acid. For practice, determine the pure calcium nitrate in the commercial substance.

Dissolve about 1 gramme of the sample in water and dilute to 100 c.c. Take 20 c.c., add 40 c.c. of N/10 oxalic acid solution and make alkaline with ammonia. Bring to the boil, allow to cool, filter off the precipitated calcium oxalate and wash the precipitate well with hot water. Mix the filtrate and washings, add sulphuric acid in slight excess, warm and titrate with N/10 potassium permanganate solution.

The number of c.c. of N/10 potassium permanganate subtracted from 40 gives the amount of N/10 oxalic acid solution required to precipitate the calcium.

The reactions taking place are represented by the equations—

$$H_2C_2O_4 + Ca(NO_3)_2 = CaC_2O_4 + 2HNO_3.$$
$$HNO_3 + NH_4OH = NH_4NO_3 + H_2O,$$

whence

$$5Ca(NO_3)_2 = 2KMnO_4 = 10H.$$

$\therefore$ 82 grammes = 1 gramme = 1,000 c.c. N. solution.

·0082 gramme = 1 c.c. N/10 solution.

(*b*) This method possesses the advantage that the strength of the oxalic acid solution need not be known. The calcium is precipitated as oxalate as in (*a*); the precipitate is then collected and dissolved in hydrochloric acid; sulphuric acid is then added and the

liberated oxalic acid titrated with standard potassium permanganate solution.

If the precipitate is not dissolved up before adding sulphuric acid there is a possibility that some particles of calcium oxalate may become coated with calcium sulphate and thus escape decomposition. A large amount of hydrochloric acid must not be used for the reason given on p. 60.

Find the proportion of calcium in Iceland spar.

Dissolve about 0·5 gramme of powdered Iceland spar in a little hydrochloric acid and make up the solution to 100 c.c. To 20 c.c. of the solution add excess of oxalic acid, make alkaline with ammonia solution and heat to boiling. Allow the liquid to cool, collect the calcium oxalate on a filter and wash with hot water till the washings are free from oxalic acid. Dissolve the precipitate in the *least possible quantity* of warm hydrochloric acid, dilute with water, add a little sulphuric acid, heat to 60° C. and titrate with N/10 potassium permanganate solution.

From the equations already given

$5Ca = 2KMnO_4 = 10H.$

$\therefore$ 20 grammes = 1 gramme = 1,000 c.c. N. solution.

0·002 gramme = 1 c.c. N/10 ,,

These two methods are also applicable for the determination of barium and strontium salts, and also, with slight modifications, for the determination of lead salts.

Ferrous Oxalate.

When sulphuric acid is added to a solution of ferrous oxalate we may suppose that ferrous sulphate and oxalic acid are formed according to the equation

$$FeC_2O_4 + H_2SO_4 = FeSO_4 + H_2C_2O_4.$$

The action of potassium permanganate on the solution is to oxidise the ferrous iron to the ferric state and the oxalic acid to carbon dioxide and water. From the equations already given

$$10FeSO_4 = 2KMnO_4 \text{ and } 10H_2C_2O_4 = 4KMnO_4,$$

whence $10FeC_2O_4 = 6KMnO_4$.

For the action of potassium permanganate on ferrous oxalate in presence of sulphuric acid, the following equation may now be written

$$10FeC_2O_4 + 6KMnO_4 + 24H_2SO_4 = 5Fe_2(SO_4)_3 + 3K_2SO_4 + 6MnSO_4 + 20CO_2 + 24H_2O.$$

$$10FeC_2O_4.2H_2O = 6KMnO_4 = 30H.$$

1,800 grammes = 30 grammes.

60 ,, = 1 gramme = 1,000 c.c. N. solution.

0·006 gramme = 1 c.c. N/10 solution.

Weigh out 0·6 gramme of hydrated ferrous oxalate, dissolve in a little dilute sulphuric acid and dilute to 100 c.c. Titrate 20 c.c. with N/10 potassium permanganate solution as directed for oxalic acid.

Back Titrations.

A standard solution of ferrous iron may be used by back titration for the determination of certain oxidising agents, such as potassium chlorate or bleaching powder, which cannot be conveniently titrated with it directly. The method consists in acting upon an excess of the ferrous salt with the oxidising agent and titrating the excess of ferrous iron with a standard solution of potassium permanganate or dichromate. The amount of

ferrous iron which has reacted with the oxidising agent is obtained by difference.

Potassium Chlorate.

When potassium chlorate is boiled with a solution of ferrous sulphate acidified with sulphuric acid it is reduced to the chloride and an equivalent amount of iron is raised to the ferric state.

From the equations

$$KClO_3 = KCl + 3O$$

and $6FeSO_4 + KClO_3 + 4H_2SO_4 = 3Fe_2(SO_4)_3 + KHSO_4 + HCl + 3H_2O.$

$$KClO_3 = 3O = 6H.$$

122·5 grammes = 6 grammes.
20·42 ,, = 1 gramme = 1,000 c.c. N. sol.
0·002042 gramme = 1 c.c. N/10 ,,

Weigh out 1 gramme of potassium chlorate and dissolve it in sufficient water to produce 100 c.c. Prepare a solution of ferrous iron by dissolving 3 grammes of ferrous sulphate in 10 c.c. of air-free water and adding sufficient sulphuric acid to make 100 c.c. after cooling. Titrate 25 c.c. of this solution with N/10 potassium permanganate solution. Boil 10 c.c. of the potassium chlorate solution with 25 c.c. of the acidified solution of ferrous sulphate for ten minutes in a flask fitted with a Bunsen valve. Cool the liquid, add 1 gramme of manganous sulphate and titrate with N/10 potassium permanganate solution. The difference between the two readings of potassium permanganate solution gives the volume of N/10 solution of ferrous iron which has been oxidised by 0·1 gramme of the sample of potassium chlorate.

Potassium Permanganate.—The official salt should contain at least

99 per cent. of the pure substance. The purity is determined by titration against a standard solution of oxalic acid.

Weigh out 0·4 gramme of the sample and dissolve in sufficient water to produce 100 c.c. Titrate 20 c.c. of N/10 oxalic acid solution with the potassium permanganate solution as described on p. 59.

Hydrogen Peroxide.—The solution of hydrogen peroxide of the British Pharmacopœia should yield from nine to eleven times its volume of oxygen when treated with solution of copper ammonio-sulphate, corresponding to from 2·72 to 3·35 grammes of H_2O_2 in 100 c.c. The determination may also be made by titrating with standard potassium permanganate solution in presence of sulphuric acid.

The reaction is represented by the equation

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2,$$

whence $5H_2O_2 = 2KMnO_4 = 10H$.

170 grammes = 10 grammes.

17 „ = 1 gramme = 1,000 c.c. N. solution.

0·0017 gramme = 1 c.c. N/10 „

Take 10 c.c. of the sample and dilute to 100 c.c. Take 10 c.c., dilute well, add sulphuric acid and titrate with N/10 potassium permanganate solution until a permanent pink colour is obtained.

The volume of oxygen yielded by the solution is calculated in the following way :—

H_2O_2 yields O.

34 grammes = 16 grammes, which occupy 11·16 litres at N. T. P.

0·0017 gramme = 0·0008 gramme, which occupies 0·558 c.c. at N. T. P.

i.e., for each c.c. of N/10 potassium permanganate solution used, 0·558 c.c. of oxygen (measured at N. T. P.) is liberated from the hydrogen peroxide.

Sodium Perborate.—This salt when treated with water yields hydrogen peroxide and sodium metaborate, thus

$$NaBO_3 + H_2O = NaBO_2 + H_2O_2.$$

It usually contains about 86·5 per cent. of $NaBO_3.4H_2O$, which corresponds to 9 per cent. by weight of available oxygen. The determination is made by means of potassium permanganate as described under hydrogen peroxide.

$NaBO_3.4H_2O = H_2O_2 = O = 2H.$

154 grammes = 16 grammes = 2 grammes.

77 „ = 8 „ = 1 gramme = 1,000 c.c. N. solution.

0·0077 gramme = 0·0008 gramme = 1 c.c. N/10 solution.

Take about 0·2 gramme, dissolve in about 50 c.c. of water, add sulphuric acid and titrate with N/10 potassium permanganate.

Sodium Nitrite.—Nitrous acid and nitrites are oxidised by potassium permanganate in presence of sulphuric acid. The oxidation takes place slowly in the cold, but much more rapidly when the solution is warmed to about 40° C. When nitrous acid or an acidified solution of a nitrite is warmed, decomposition takes place with evolution of nitrogen peroxide. The usual order is therefore reversed in this titration, and the nitrite solution is added from a burette to a warm acidified solution of potassium permanganate.

The reactions taking place in the case of sodium nitrite are expressed thus

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + 2HNO_2.$$

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O.$$

$5NaNO_2 = 2KMnO_4 = 10H.$

5×69 grammes		= 10 grammes.
34·5	,, = 1 gramme	= 1,000 c.c. N. solution.
0·00345 gramme		= 1 c.c. N/10 ,,

Weigh out about 0·7 gramme of the sample and dissolve in sufficient water to produce 100 c.c. Measure out 50 c.c. of N/10 potassium permanganate solution; acidify strongly with sulphuric acid and warm to 40–50° C. Add the nitrite solution slowly from the burette with constant shaking until the potassium permanganate solution is just decolorised.

At least 95 per cent. of the pure salt should be present.

The determination may also be carried out by a process of residual titration. The sodium nitrite is oxidised by means of an excess of potassium permanganate solution and sulphuric acid, the mixture being heated to 40° and allowed to stand for five minutes.

The excess of potassium permanganate is then determined by means of standard oxalic acid solution.

Ferrous Sulphate.—The official salt should contain at least 97·5 per cent. of the pure hydrate $FeSO_4.7H_2O$. The purity is determined by titration with N/10 potassium permanganate solution. From the equation on p. 58, 0·0278 gramme of $FeSO_4.7H_2O$ = 1 c.c. N/10 solution.

Weigh out about 3 grammes of the sample and dissolve in sufficient air-free water to make 100 c.c. Take 20 c.c., add dilute sulphuric acid, and titrate with N/10 potassium permanganate solution.

Exsiccated Ferrous Sulphate.—This preparation consists of the

monohydrate $FeSO_4.H_2O$ with some ferric oxysulphate and is required to contain at least 77 per cent. of pure anhydrous ferrous sulphate. 0·0152 gramme of $FeSO_4$ = 1 c.c. N/10 solution.

It is determined in the same way as ferrous sulphate, but the addition of a little sulphuric acid is necessary in preparing the solution.

Reduced Iron.—Reduced iron is prepared by heating ferric hydroxide to dull redness in a current of dry hydrogen. It consists of metallic iron mixed with oxides of iron. The amount of free iron should not be less than 80 per cent. The medicinal value is supposed to be due to the metallic iron it contains, and the process of determination is designed to exclude iron in the combined state. The sample is shaken with a solution of copper sulphate, when the metallic iron is dissolved to form ferrous sulphate and copper is precipitated, according to the equation

$$Fe + CuSO_4 = Cu + FeSO_4.$$

The copper sulphate does not act upon the oxides of iron.

The copper and oxides of iron are filtered off as rapidly as possible to avoid atmospheric oxidation, and the filtrate is titrated with standard potassium permanganate solution.

From the equations already given

0·0056 gramme Fe = 1 c.c. N/10 solution.

Weigh about 1 gramme of the sample into a flask containing a hot solution of 5 grammes of copper sulphate in 80 c.c. of water. Shake occasionally during ten minutes, keeping the mixture hot, filter rapidly, cool to room temperature, and make up the filtrate to 100 c.c. with air-free water. Take 20 c.c., add dilute sulphuric acid, and titrate with N/10 potassium permanganate solution.

Lead Acetate.—The official salt should contain not less than 99·5 per cent. of the pure hydrate $Pb(C_2H_3O_2)_2.3H_2O$. The method of determination is similar to the second of the two processes described for calcium in this chapter (*see* p. 64). Ammonia is not added in this case because lead oxalate is appreciably soluble in solutions containing ammonia or ammonium salts, but the oxalate is precipitated from a solution made acid with acetic acid, lead oxalate being insoluble in this acid. For the titration the precipitate is dissolved in dilute nitric acid since hydrochloric acid would form the relatively insoluble chloride and some particles of the lead oxalate might become coated with the chloride and remain undecomposed.

The reactions taking place are represented by the equations

$$Pb(C_2H_3O_2)_2 + H_2C_2O_4 = PbC_2O_4 + 2HC_2H_3O_2.$$

$$PbC_2O_4 + 2HNO_3 = Pb(NO_3)_2 + H_2C_2O_4.$$

$5Pb(C_2H_3O_2)_2.3H_2O = 5H_2C_2O_4 = 10H.$
1,895 grammes = 10 grammes.
189·5 ,, = 1 gramme = 1,000 c.c. N. sol.
0·01895 gramme = 1 c.c. N/10 ,,

Weigh out about 0·5 gramme of the salt, dissolve in water acidified with acetic acid, add excess of oxalic acid and heat to boiling. Allow the liquid to cool, collect the precipitate and wash with hot water until the washings no longer contain oxalic acid. Dissolve the precipitate in a small quantity of dilute nitric acid, add excess of dilute sulphuric acid, heat to 60° C., and titrate with N/10 potassium permanganate solution.

The determination may also be made by the first method described for calcium on p. 63, the lead salt being dissolved in freshly boiled distilled water and the addition of ammonia being omitted.

Strong Solution of Lead Subacetate.—The lead in this preparation is determined in the same way as in lead acetate.

One gramme should be taken for each titration. 17·6 per cent. of lead, Pb, should be present. 0·01035 gramme of Pb = 1 c.c. N/10 solution.

CHAPTER VIII

DETERMINATIONS INVOLVING OXIDATION AND REDUCTION (*continued*)

Potassium Dichromate.

In presence of sulphuric acid and a suitable reducing agent potassium dichromate acts according to the equation

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

One molecule of potassium dichromate thus yields three "available" atoms of oxygen. The oxidising action may be regarded as the conversion of chromic anhydride, CrO_3, into chromic oxide, Cr_2O_3. Thus

$$2CrO_3 = Cr_2O_3 + 3O.$$

since $K_2Cr_2O_7 = 3O = 6H.$

294 grammes = 6 grammes.

49 ,, = 1 gramme = 1,000 c.c. N. sol.

A normal solution of potassium dichromate thus contains one-sixth of the gramme molecular weight in 1,000 c.c.

A decinormal solution is usually employed.

Weigh out 4·9 grammes of the salt and dissolve in sufficient water to produce 1,000 c.c.

The solution should be standardised by means of ferrous ammonium sulphate.

Combining the equations for the reduction of potassium dichromate and for the oxidation of ferrous sulphate the following is obtained :—

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O.$$

The chromium sulphate produced gives a blue colour to the solution, and since there is no sharp change of colour when the oxidation is complete, an indicator must be used. The substance employed for this purpose is potassium ferricyanide, $K_3Fe(CN)_6$, which in dilute solution gives a blue colour, Turnbull's blue, with ferrous salts, according to the equation.

$$2K_3Fe(CN)_6 + 3FeSO_4 = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4.$$

With ferric salts only a pale yellow colour is produced. The indicator is not added to the solution to be titrated, but is used " externally." A portion of the liquid in the flask is removed at intervals and mixed with a little of the ferricyanide solution, when so long as any ferrous salt remains unoxidised a blue colour is obtained, and the completion of the oxidation is shown by the non-appearance of the blue colour.

Potassium ferricyanide decomposes on keeping and the crystals become coated with potassium ferrocyanide. The presence of ferrocyanide in the solution used as indicator is undesirable because it gives a blue colour, Prussian blue, with ferric salts according to the equation

$$2Fe_2(SO_4)_3 + 3K_4Fe(CN)_6 = Fe_4[Fe(CN)_6]_3 + 6K_2SO_4,$$

and the end-point is thus obscured.

A large crystal of ferricyanide should be taken and

washed free from ferrocyanide before dissolving. The solution should be freshly prepared for use, as it decomposes on keeping, forming the ferrocyanide.

The standardisation is conducted in the following way :—

By means of a glass rod place a series of drops of the potassium ferricyanide solution on a white porcelain tile. Measure out 20 c.c. of N/10 solution of ferrous ammonium sulphate, prepared as described on p. 58, add a little dilute sulphuric acid and run in the dichromate solution from the burette. At intervals remove a drop of liquid from the flask by means of a glass rod and apply it to one of the drops on the tile. The titration is complete when a blue colour is no longer produced. The factor of the N/10 potassium dichromate solution is then calculated in the usual way.

Potassium dichromate is used for the determination of iron salts. It possesses the advantage over potassium permanganate that it may be used in presence of phosphoric acid or of hydrochloric acid without special precautions.

Ferric Chloride.

The iron is reduced to the ferrous state by means of zinc and hydrochloric acid, and the solution is then titrated with standard potassium dichromate solution. The reduction takes place according to the equation

$$FeCl_3 + H = FeCl_2 + HCl.$$

The reaction between ferrous chloride and potassium dichromate is expressed by the equation

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2CrCl_3 + 2KCl + 7H_2O,$$

whence

$6FeCl_3 = K_2Cr_2O_7 = 6H.$

975 grammes = 6 grammes.

162·5 ,, = 1 gramme = 1,000 c.c. N. sol.

0·01625 gramme = 1 c.c. N/10 ,,

For practice, determine the anhydrous ferric chloride in the bench reagent which contains about 3 to 5 per cent. of the hydrated salt, $FeCl_36H_2O$.

Measure out 30 c.c. of the solution and reduce with zinc and sulphuric acid as described on p. 62. When the reduction is complete, filter, wash and dilute to 100 c.c. with air-free water. Take 50 c.c., add a little hydrochloric acid if necessary, and titrate with N/10 potassium dichromate solution, using potassium ferricyanide externally as indicator.

Potassium Chromate.

In presence of sulphuric or hydrochloric acid, potassium chromate acts as an oxidising agent in the same way as the dichromate

$$2K_2CrO_4 + 5H_2SO_4 = 2K_2SO_4 + Cr_2(SO_4)_3 + 5H_2O + 3O.$$

The purity of potassium chromate may therefore be found by titration against a standard solution of ferrous iron.

$$2K_2CrO_4 + 6FeSO_4 + 8H_2SO_4 = 2K_2SO_4 + 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 8H_2O,$$

whence

$2K_2CrO_4 = 6FeSO_4 = 6H.$

388 grammes = 6 grammes.

64·67 ,, = 1 gramme = 1,000 c.c. N. sol.

0·006467 gramme = 1 c.c. N/10 ,,

Weigh out 0·7 gramme of the salt and dissolve in sufficient water to produce 100 c.c. Place the solution in the burette and titrate into 20 c.c. of acidified N/10

ferrous ammonium sulphate solution, using potassium ferricyanide as external indicator.

Bleaching Powder may be regarded as a mixture of the compound Ca(OCl)Cl with calcium hydroxide. The liquid obtained by treatment with water contains calcium chloride and calcium hypochlorite, and the activity of bleaching powder is believed to be due to the nascent oxygen yielded by the hypochlorite. In determining the value of bleaching powder it is usual to measure its oxidising power by means of some reducing agent such as a ferrous salt (see below), arsenious oxide (p. 86), or potassium iodide (p. 90), and to express the result in terms of the chlorine equivalent to the nascent oxygen. This is termed the "available chlorine."

Available Chlorine.

The available chlorine in bleaching powder may be determined by allowing it to react with an excess of an acidified standard solution of ferrous iron and titrating the excess of ferrous iron with standard potassium dichromate solution. The following equations represent the oxidation :—

$$Ca(OCl)Cl + H_2SO_4 = CaSO_4 + HOCl + HCl$$
$$HOCl + HCl = H_2O + Cl_2$$
$$2FeSO_4 + H_2SO_4 + Cl_2 = Fe_2(SO_4)_3 + 2HCl.$$

whence Cl = Fe = H.

35·5 grammes = 1 gramme = 1,000 c.c. N. sol.
0·00355 gramme = 1 c.c. N/10 ,,

Weigh out about 10 grammes of the powder. Triturate in a mortar with successive small quantities of water and transfer the liquids to a 1,000 c.c. flask. Continue the

treatment with water until all the powder has been conveyed to the flask, then dilute to 1,000 c.c. and shake thoroughly. Measure 20 c.c. of the milky fluid, add it to 40 c.c. of N/10 ferrous ammonium sulphate solution acidified with sulphuric acid, mix the liquids well and titrate back with N/10 potassium dichromate solution.

In making the solution of bleaching powder care must be taken to grind the powder finely, so as to ensure complete solution of the chloride and hypochlorite. The liquid is usually turbid from the presence of excess of calcium hydroxide. The solution must be titrated immediately, as it rapidly undergoes decomposition.

This method has the disadvantage that if the bleaching powder contains any calcium chlorate, as is often the case, this salt is decomposed by the acid with liberation of chlorine. The proportion of chlorine found is then too high and does not correctly represent the activity of the powder which, as stated above, depends on the proportion of hypochlorite present.

Saccharated Iron Phosphate.—The preparation of the British Pharmacopœia consists of ferrous phosphate, ferric phosphate and ferric oxide mixed with glucose. It is required to contain at least 60 per cent. of ferrous salts calculated as hydrated ferrous phosphate, $Fe_3(PO_4)_2.8H_2O$. The proportion of ferrous salt present is found by dissolving in hydrochloric, sulphuric or phosphoric acid and titrating with standard potassium dichromate solution.

The glucose present exerts a reducing action which may render the results too high. The error should be minimised by conducting the titration quickly.

From the equations

$$Fe_3(PO_4)_2 + 6HCl = 3FeCl_2 + 2H_3PO_4.$$

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2CrCl_3 + 2KCl + 7H_2O.$$

$Fe_3(PO_4)_2 8H_2O = 3FeCl_2 = 3H.$

502 grammes = 3 grammes.

167·3 ,, = 1 gramme = 1,000 c.c. N. solution.

0·01673 gramme = 1 c.c. N/10 ,,

Take 3 grammes of the sample, dissolve in dilute hydrochloric acid, and make the volume up to 100 c.c. with air-free water. Titrate 20 c.c. with N/10 potassium dichromate solution, using potassium ferricyanide as indicator.

Saccharated Iron Carbonate.—The preparation is a mixture of ferrous carbonate and hydroxide, ferric oxide and glucose. The ferrous iron calculated as carbonate, $FeCO_3$, should form at least 50 per cent. of the mixture. The sample is dissolved in phosphoric, hydrochloric or sulphuric acid and titrated with standard potassium dichromate solution. Ferrous phosphate is produced according to the equations

$$3FeCO_3 + 2H_3PO_4 = Fe_3(PO_4)_2 + 3CO_2 + 3H_2O.$$
$$3Fe(OH)_2 + 2H_3PO_4 = Fe_3(PO_4)_2 + 6H_2O.$$

The oxidation is expressed by the equation

$$2Fe_3(PO_4)_2 + K_2Cr_2O_7 + 5H_3PO_4 = K_2HPO_4 + 2CrPO_4 + 6FePO_4 + 7H_2O.$$

The titration should be conducted quickly, so as to avoid as far as possible the reducing effect of glucose.

$$FeCO_3 = H.$$
$$116 \text{ grammes} = 1 \text{ gramme} = 1{,}000 \text{ c.c. N. solution.}$$
$$0{\cdot}0116 \text{ gramme} = 1 \text{ c.c. N/10 ,,}$$

Take about 3 grammes of the sample, dissolve in excess of concentrated phosphoric acid, and dilute with air-free water to 100 c.c. Titrate 20 c.c. with N/10 potassium dichromate solution, using potassium ferricyanide as external indicator.

Chromic Anhydride.—On p. 72, it is pointed out that the oxidising action of potassium dichromate is due essentially to the change of chromic anhydride into chromic oxide, thus :—

$$2CrO_3 = Cr_2O_3 + 3O.$$

Use is made of this change for the determination of chromic anhydride itself. The reaction between this substance and ferrous sulphate is represented by the equation

$$2CrO_3 + 6FeSO_4 + 6H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6H_2O,$$

whence $2CrO_3 = 6FeSO_4 = 6H.$

$$200 \text{ grammes} = 6 \text{ grammes.}$$
$$33{\cdot}33 \text{ ,,} = 1 \text{ gramme} = 1{,}000 \text{ c.c. N. solution.}$$
$$0{\cdot}003333 \text{ gramme} = 1 \text{ c.c. N/10 ,,}$$

Weigh out about 0·4 gramme of the crystals and dissolve in sufficient water to make 100 c.c. Take 20 c.c. of N/10 ferrous ammonium

sulphate solution, add sulphuric acid, and titrate with the chromic acid solution, using potassium ferricyanide as external indicator.

The crystals are very deliquescent and must be weighed in a stoppered bottle.

Solution of Chromic Acid.—The strength of this solution may be determined as described for chromic anhydride. About 1·5 grammes diluted to 100 c.c. forms a solution of suitable strength for titrating against N/10 solution of ferrous salt.

CHAPTER IX

DETERMINATIONS INVOLVING OXIDATION AND REDUCTION (*continued*)

Iodine.

In presence of a suitable reducing agent, iodine reacts with water according to the equation

$$I_2 + H_2O = 2HI + O,$$

whence $I_2 = O = 2H.$

$$254 \text{ grammes} = 2 \text{ grammes.}$$

$$127 \quad ,, \quad = 1 \text{ gramme} = 1{,}000 \text{ c.c. N. sol.}$$

Thus a normal solution of iodine contains the gramme-atomic weight in 1,000 c.c.

Pure iodine is prepared by heating the commercial substance with potassium iodide and collecting the crystalline sublimate. Any chlorine or bromine present is removed by interaction with the potassium iodide, thus :—

$$2KI + Cl_2 = 2KCl + I_2.$$

Iodine is only slightly soluble in water, but the solubility is greatly increased by the addition of potassium iodide, probably owing to the formation in the solution of a compound, KI_3. This compound, however, is very unstable and the solution behaves towards reducing agents as though it contained only free iodine and potassium iodide.

Iodine should always be weighed in a stoppered bottle. The substance volatilises at ordinary temperatures, and the vapour attacks the metal of the balance. The stopper should not be removed while the bottle is inside the balance case.

A decinormal solution is usually employed.

Weigh out 12·7 grammes of pure iodine into a 1,000 c.c. flask, add 20 grammes of pure potassium iodide and about 200 c.c. of water. Shake the flask until the iodine is all dissolved, then fill up to the mark on the neck with distilled water.

The volatile nature of iodine makes it difficult to weigh out exactly the amount required, and the solution may not be precisely the correct strength. It should therefore be standardised by means of pure arsenious oxide.

The solution should be kept in a cool, dark place and in a stoppered bottle. Even under these conditions the strength of the solution diminishes with keeping, and the standardisation should be repeated at frequent intervals.

Standardisation.

Arsenious anhydride, when oxidised, is converted into arsenic oxide, thus :—

$$As_4O_6 + 2O_2 = 2As_2O_5.$$

Combining this with the equation given for the reduction of iodine, the following is obtained :—

$$As_4O_6 + 4H_2O + 4I_2 = 2As_2O_5 + 8HI,$$

whence $As_4O_6 = 4O = 8H$.

396 grammes = 8 grammes.

49·5 „ = 1 gramme = 1,000 c.c. N. sol.

The reaction is reversible, and if iodine is simply added to a neutral solution of arsenious oxide, a state of equilibrium is reached before the oxidation is com-

plete. In order to prevent this, sufficient sodium bicarbonate must be added to combine with the arsenic oxide and hydriodic acid, forming sodium arsenate and sodium iodide, which do not react with one another. Sodium hydroxide or carbonate cannot be used instead of the bicarbonate for this purpose, as they combine with iodine to form sodium iodide and sodium iodate, thus :—

$$6NaOH + 3I_2 = 5NaI + NaIO_3 + 3H_2O.$$

$$3Na_2CO_3 + 3I_2 = 5NaI + NaIO_3 + 3CO_2.$$

The completion of the oxidation is shown by the appearance of a pale yellow colour due to a slight excess of iodine. The end-point is made more evident by the addition of starch water, which gives an intense blue colour with free iodine, at ordinary temperatures. The starch water is best prepared in the following way :— One gramme of starch powder is well mixed with 10 c.c. of cold water and then added, with constant stirring, to sufficient boiling water to produce about 200 c.c. The mixture is then boiled for a few minutes and, after cooling, filtered for use. It should be freshly prepared.

Arsenious oxide is only slightly soluble in water, but it dissolves readily in solution of sodium hydroxide, forming sodium arsenite. For the reasons mentioned above, any excess of sodium hydroxide must be neutralised with hydrochloric acid, and the solution then made alkaline with sodium bicarbonate before titrating.

Prepare a N/10 solution of arsenious oxide by dissolving 0·495 gramme of the pure substance in a little strong solution of sodium hydroxide, and diluting to 100 c.c. Take 20 c.c., add dilute hydrochloric acid until the liquid is slightly acid, then excess of sodium bicarbonate and about 50 c.c. of water.

Run in the iodine solution from the burette until the brown colour disappears slowly on shaking, then add starch water, and titrate until a permanent blue colour is obtained. A slight excess of sodium bicarbonate must be maintained throughout the titration. The sodium bicarbonate should be free from carbonate, and the conditions of the titration should be such as to minimise the formation of carbonate by dissociation, *i.e.*, the liquid should be cool and well diluted, and the titration should be conducted quickly.

If the starch water is added at the beginning of the titration, dark blue flocks may be formed and the end-point is not so clear. The factor of the iodine solution is calculated in the usual way.

Antimonious Oxide.

Antimonious oxide is determined by titration with standard iodine solution in the same way as for arsenious oxide. The oxidation takes place in accordance with the equation

$$Sb_4O_6 + 4H_2O + 4I_2 = 2Sb_2O_5 + 8HI,$$

whence $Sb_4O_6 = 8I = 8H$.

576 grammes = 8 grammes.
72 ,, = 1 gramme = 1,000 c.c. N. sol.
·0072 gramme = 1 c.c. N/10 ,,

The oxide dissolves readily in sodium hydroxide solution just as arsenious oxide does, but when the solution is neutralised with hydrochloric acid and sodium bicarbonate added, the antimonious oxide is reprecipitated. The same objection holds if the oxide is dissolved in hydrochloric acid.

Antimonious oxide dissolves in hot solution of potas-

sium hydrogen tartrate with formation of tartar emetic, thus :—

$$4KHC_4H_4O_6 + Sb_4O_6 = 4K(SbO)C_4H_4O_6 + 2H_2O.$$

Prolonged boiling is sometimes necessary to produce a clear solution, and the potassium salt may be replaced with advantage by tartaric acid or sodium potassium tartrate, with which antimonious oxide combines to give a compound similar to tartar emetic. These solutions do not give a precipitate of antimonious oxide when sodium bicarbonate is added, except after standing for some time.

The most rapid method is to dissolve the oxide in concentrated hydrochloric acid, in which it dissolves readily in the cold, with the addition of a little tartaric acid to prevent precipitation when the solution is made alkaline.

Take about 1 gramme of the sample, dissolve in a few c.c. of concentrated hydrochloric acid, and add 1·5 grammes of tartaric acid. Dilute to 100 c.c. and measure 20 c.c. into the titrating flask. Add sodium hydroxide solution until the liquid is only slightly acid, then add excess of sodium bicarbonate and titrate with N/10 iodine solution, using starch water as indicator. An excess of sodium bicarbonate must be maintained throughout the titration.

For pharmaceutical purposes antimonious oxide should contain 99·36 per cent. of the pure substance.

Sulphur Dioxide.

In aqueous solution sulphur dioxide readily combines with oxygen and water to form sulphuric acid, thus :—

$$SO_2 + H_2O + O = H_2SO_4.$$

The oxidation is brought about at ordinary temperature by the addition of iodine solution, and this reaction

is made the basis of the determination of sulphur dioxide. Combining the above equation with that given on p. 80 for the reduction of iodine

$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4,$$

whence $SO_2 = 2I = 2H$.

64 grammes $= 2$ grammes.

32 ,, $= 1$ gramme $= 1,000$ c.c. N. sol.

·0032 gramme $=$ 1 c.c. N/10 ,,

Sulphuric acid, however, attacks hydriodic acid at ordinary temperatures with formation of sulphur dioxide and iodine, *i.e.*, the above reaction is reversible. The oxidation is complete only when the concentration of the sulphur dioxide does not exceed 0·05 per cent.

In finding the strength of a solution of sulphur dioxide, a rough determination is first made and the solution diluted in accordance with the result. As the solution rapidly takes up atmospheric oxygen, exposure to air must be avoided as far as possible, and air-free water must be used for diluting.

Adjust the strength of the solution so that it contains about 0·4 per cent. of sulphur dioxide. Take 10 c.c., add at least 100 c.c. of water, and titrate with N/10 iodine solution, using starch water as indicator.

Barium Thiosulphate.

This substance reacts with iodine to form barium iodide and tetrathionate, according to the equation

$$2BaS_2O_3 + I_2 = BaI_2 + BaS_4O_6,$$

whence

$2BaS_2O_3.H_2O = 2I = 2H$.

535 grammes $= 2$ grammes.

267·5 ,, $= 1$ gramme $= 1,000$ c.c. N. sol.

·02675 gramme $=$ 1 c.c. N/10 ,,

The purity of the commercial substance is found by titration with standard iodine solution As the salt is not very soluble in water, it is titrated in suspension, and the flask must be well shaken during the operation.

Weigh about 0·5 gramme of the sample into a stoppered bottle and add about 50 c.c. of water. Titrate with N/10 iodine solution, shaking vigorously after each addition. When about 15 c.c. of iodine have been run in, add a little starch water and continue the titration until a blue colour is produced which persists after shaking and standing for five minutes.

Arsenious Iodide.

In alkaline solution this compound is completely hydrolysed thus :—

$$4AsI_3 + 6H_2O = As_4O_6 + 12HI.$$

The purity may be determined by titrating the arsenious oxide produced with standard iodine solution.

$$4AsI_3 = As_4O_6 = 8H.$$

$$4 \times 456 \text{ grammes} = 8 \text{ grammes.}$$

$$228 \quad \text{,,} \quad = 1 \text{ gramme.}$$

$$\cdot 0228 \text{ gramme} = 1 \text{ c.c. N/10 solution.}$$

Weigh out 2·5 grammes, dissolve in an aqueous solution of sodium bicarbonate and make up to 100 c.c. Take 20 c.c. and titrate with N/10 iodine solution, adding a slight excess of sodium bicarbonate.

A determination of the iodide may also be made by the method described on p. 110.

Bleaching Powder.

Arsenious oxide in alkaline solution is oxidised by chlorine in the same way as by iodine. Thus

$$4Cl_2 + As_4O_6 + 4H_2O = 2As_2O_5 + 8HCl.$$

The reaction may be used for the determination of the available chlorine in bleaching powder. An excess of a standard solution of arsenious oxide is treated with a solution of the bleaching powder, and the excess of arsenious oxide is then titrated with a standard solution of iodine. From the above equation

$$4Cl_2 = As_4O_6 = 4O = 8H.$$

$8 \times 35{\cdot}5$ grammes	$= 8$ grammes.
$35{\cdot}5$,,	$= 1$ gramme.
$\cdot 00355$ gramme	$= 1$ c.c. N/10 solution.

Prepare a solution of the bleaching powder as described on p. 76 and a N/10 solution of arsenious oxide as described on p. 82. Mix 20 c.c. of the bleaching powder solution with 40 c.c. of the solution of arsenious acid in the presence of excess of sodium bicarbonate, and titrate back with N/10 iodine solution, using starch water as indicator. This method has the advantage that any calcium chlorate present is not decomposed, and the chlorine determined corresponds to the hypochlorite (*cf.* pp. 77, 91).

Arsenious Anhydride.—The purity of arsenious anhydride for pharmaceutical purposes is ascertained by titration with standard iodine solution. It should contain not less than 99·8 per cent. of the pure oxide. From the equation given on p. 81, 1 c.c. of N/10 iodine solution oxidises 0·00495 gramme of arsenious oxide.

Weigh out about 0·5 gramme, dissolve in sodium hydroxide solution, make slightly acid with hydrochloric acid, and dilute to 100 c.c. Take 20 c.c., dilute well with water, add excess of sodium bicarbonate, and titrate with N/10 iodine solution, using starch water as indicator.

Arsenical Solution.—This preparation is made by dissolving arsenious oxide in solution of potassium carbonate and adding compound tincture of lavender. The solution should contain 1 gramme of arsenious oxide in 100 c.c.

An excess of potassium carbonate is present, and the solution must therefore be made acid before titrating.

Take 10 c.c. of the sample, make slightly acid with hydrochloric acid, and dilute well with water. Add excess of sodium bicarbonate and titrate with N/10 iodine solution, using starch water as indicator.

Hydrochloric Solution of Arsenic.—This solution is prepared by dissolving arsenious oxide in water containing hydrochloric acid. 100 c.c. should contain 1 gramme of arsenious oxide.

The strength is determined as for arsenical solution, except that no hydrochloric acid need be added.

Tartarated Antimony.—The official salt should contain at least 99 per cent. of the hydrate $(K(SbO)C_4H_4O_6)_2.H_2O$. The antimony present is oxidised by iodine to antimonic oxide, thus :—

$$2K(SbO)C_4H_4O_6 + 2I_2 + 3H_2O = Sb_2O_5 + 4HI + 2KHC_4H_4O_6,$$

whence

$$(K(SbO)C_4H_4O_6)_2H_2O = 2I_2 = 4H.$$

664 grammes = 4 grammes.
166 „ = 1 gramme = 1,000 c.c. N. sol.
0·0166 gramme = 1 c.c. N/10 „

Weigh out 1·5 grammes of the sample and dissolve in sufficient water to produce 100 c.c. Take 20 c.c., dilute well, add sodium potassium tartrate and excess of sodium bicarbonate, and titrate with N/10 iodine solution, using starch water as indicator.

The sodium potassium tartrate is added to prevent the precipitation of basic salts of antimony, which may take place when sodium bicarbonate is added.

Antimonial Wine.—This preparation is made by dissolving tartarated antimony in boiling water and mixing the solution with sherry.

Take 50 c.c., dilute well with water, add excess of sodium bicarbonate and titrate with N/10 solution of iodine, using starch water as indicator. 100 c.c. should contain 0·4 gramme of tartarated antimony.

Antimonial Powder.—This is a mixture of one part of antimonious oxide with two parts of calcium phosphate. The proportion of antimonious oxide is determined as described on p. 83.

CHAPTER X

DETERMINATIONS INVOLVING OXIDATION AND REDUCTION (*continued*)

Sodium Thiosulphate.

Sodium thiosulphate acts upon iodine in the same way as the barium salt.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

A standard solution of sodium thiosulphate may therefore be used for the determination of iodine. The reactions performed by direct titration with iodine solution may be carried out by adding excess and titrating back with standard thiosulphate solution. In cases where the substance is liable to oxidation by the atmosphere this is the best method. Also any compound which liberates iodine quantitatively from potassium iodide can be determined by titrating the liberated iodine with standard thiosulphate solution. Crystals of sodium thiosulphate have the composition

$$Na_2S_2O_3.5H_2O.$$

From the equation given

$2Na_2S_2O_3.5H_2O$	$= 2I = 2H.$	
496 grammes	$= 2$ grammes.	
248 ,,	$= 1$ gramme $=$	1,000 c.c. N. sol.

To make a N/10 solution, weigh out 24·8 grammes of

the pure crystals and dissolve in sufficient water to produce 1,000 c.c.

Place 20 c.c. of N/10 iodine solution in the flask and run in the thiosulphate solution until only a pale yellow colour remains. Add a little starch water and titrate until the blue colour disappears. The starch mucilage must not be added at first, or a flocculent blue precipitate is produced and is difficult to decompose.

The factor of the sodium thiosulphate solution is then calculated in the usual way.

Chlorine Water.

When free chlorine acts upon potassium iodide it liberates its equivalent of iodine, thus :—

$$Cl_2 + 2KI = I_2 + 2KCl.$$

The iodine liberated may be determined with standard sodium thiosulphate solution, and the chlorine corresponding to it can be calculated from the above equation, thus :—

$$Cl_2 = I_2 = 2H.$$

71 grammes = 2 grammes.

35·5 ,, = 1 gramme = 1,000 c.c. N. solution.

0·00355 gramme = 1 c.c. N/10 ,,

Take 10 c.c. of chlorine water, add excess of potassium iodide, and titrate with N/10 sodium thiosulphate solution, using starch water towards the end as indicator. Bromine water is determined in precisely the same way.

Bleaching Powder.

The available chlorine may be determined by adding acid in presence of potassium iodide and titrating the iodine set free by the chlorine with standard sodium thiosulphate solution.

1 c.c. N/10 thiosulphate solution $= 0{\cdot}00355$ gramme of chlorine, as above.

Take 0·25 gramme of the bleaching powder, add about 100 c.c. of water and 1 gramme of potassium iodide. Acidify and titrate with N/10 sodium thiosulphate solution, using starch water as indicator.

When hydrochloric acid or sulphuric acid is used any chlorate present is decomposed, and the result may be too high. If acetic acid is used this difficulty is avoided.

The chlorinated lime of the British Pharmacopœia is required to yield at least 30 per cent. of available chlorine.

Oxidising Agents.

Various other oxidising agents in acid solution liberate iodine quantitatively from potassium iodide. The solution may be regarded as containing hydriodic acid, and the reaction may be expressed thus :—

$$O + 2HI = H_2O + I_2.$$

A useful exercise for the student is to check the strength of the thiosulphate solution by means of the standard potassium dichromate or permanganate solution.

Potassium Dichromate.

The reaction is expressed by the equation

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI = 4K_2SO_4 + 3I_2 + Cr_2(SO_4)_3 + 7H_2O.$$

Take 20 c.c. of the N/10 potassium dichromate solution, add a little dilute sulphuric or hydrochloric acid and about 0·5 gramme of potassium iodide. Titrate with the thiosulphate solution, adding starch water towards the end as indicator.

The chromium salt produced by the reduction of the potassium dichromate gives the solution a pale blue colour, and the end-point to be noted is the change from deep blue to the pale blue of the chromium salt.

Potassium Permanganate.

The reaction is expressed by the equation

$$2KMnO_4 + 8H_2SO_4 + 10KI = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O.$$

Take 20 c.c. of the N/10 potassium permanganate solution, add dilute sulphuric acid and 0·5 gramme of potassium iodide. Titrate with the thiosulphate solution, using starch water towards the end as indicator. The reduction products of potassium permanganate give a colourless solution.

Ferric Salts.

The direct determination of ferric salts without previous reduction to the ferrous state may be effected by making use of their oxidising action on potassium iodide. In the presence of acid, ferric salts liberate iodine from potassium iodide; under suitable conditions the reaction can be made quantitative and the iodine set free can be titrated with sodium thiosulphate solution. For example, in the case of ferric chloride the reaction is expressed by the equation

$$2FeCl_3 + 2HI = 2FeCl_2 + 2HCl + I_2.$$

The liberation of iodine takes some considerable time to reach completion at ordinary temperatures, but if the reaction mixture is kept at a temperature of 40° the decomposition is completed in about thirty minutes. The reaction should be carried out in a glass-stoppered bottle, so that no iodine may be lost by volatilisation.

For practice determine the pure ferric chloride in the hydrated salt. From the above equation

$2FeCl_3 = I_2 = 2H.$

325 grammes = 2 grammes.

162·5 ,, = 1 gramme = 1,000 c.c. N. solution.

0·01625 gramme = 1 c.c. N/10 ,,

Weigh out about 1·25 grammes of the sample and dissolve it in sufficient water to produce 100 c.c. Place 20 c.c. in a bottle, add about 3 c.c. of hydrochloric acid and 4 grammes of potassium iodide and close the bottle securely with a glass stopper. Keep the mixture at 40° for thirty minutes, cool, dilute well and titrate with N/10 sodium thiosulphate solution, using starch water as indicator.

Copper Sulphate.

The reaction between potassium iodide and copper sulphate in solution results in the precipitation of cuprous iodide and liberation of iodine, according to the equation

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4.$$

Cupric iodide may be supposed to be formed by double decomposition and to split up at once into cuprous iodide and iodine.

$$2CuSO_4 + 4KI = 2K_2SO_4 + 2CuI_2.$$

$$2CuI_2 = Cu_2I_2 + I_2.$$

Copper sulphate may therefore be determined by titration of the iodine with standard thiosulphate solution. Thus :—

$2CuSO_4.5H_2O = I_2 = 2H.$

499 grammes = 2 grammes.

249·5 ,, = 1 gramme = 1,000 c.c. N. sol.

0·02495 gramme = 1 c.c. N/10 ,,

The result is not accurate if any free acid except acetic acid is present. The solution must be made slightly alkaline by adding sodium carbonate until the solution is cloudy, and then made clear again by the cautious addition of acetic acid. The solution of copper should be fairly concentrated, and a large excess of potassium iodide must be used, or the reaction is not complete.

Weigh out about 3 grammes of crystalline copper sulphate, dissolve in water, neutralise with sodium carbonate and acetic acid as described above, and make up to 100 c.c. Take 20 c.c., add about 6 grammes of potassium iodide, and titrate the iodine liberated with N/10 sodium thiosulphate solution, using starch water as indicator.

Sulphur Dioxide by Back Titration.

The results obtained by direct titration of sulphur dioxide in solution are usually too low owing to the volatilisation of the sulphur dioxide during titration and also to the oxidising action of the air. This error is avoided if the solution is added to an excess of standard iodine solution and the excess then found by titration with standard sodium thiosulphate solution.

The sulphur dioxide solution should be delivered from a pipette with the point dipping below the surface of the iodine solution.

Iodine.—Iodine used for pharmaceutical purposes is required to contain at least 99 per cent. of the pure substance. The purity is determined by means of standard sodium thiosulphate solution. From the equation already given 0·0127 gramme of iodine = 1 c.c. N/10 solution.

Weigh out 1 gramme of the sample in a stoppered bottle and dissolve it in 20 c.c. of water containing about 2 grammes of potassium iodide. Dilute to 100 c.c. and titrate 20 c.c. with N/10 sodium thiosulphate solution, adding starch water towards the end as indicator.

Weak Tincture of Iodine.—Take 10 c.c., dilute with water, and titrate with N/10 sodium thiosulphate solution, using starch water as indicator. 100 c.c. should contain between 2·44 and 2·51 grammes of pure iodine.

Strong Tincture of Iodine.—Dilute 10 c.c. with sufficient water to make 100 c.c. and titrate 20 c.c. as for the weak tincture. 100 c.c. should contain between 9·75 and 10·06 grammes of pure iodine.

Chromic Anhydride.—The iodometric method described on p. 91 for potassium dichromate may be employed for the determination of chromic anhydride. The liberation of iodine takes place according to the equation

$$2CrO_3 + 6H_2SO_4 + 6KI = 3I_2 + Cr_2(SO_4)_3 + 3K_2SO_4 + 6H_2O,$$

whence $2CrO_3 = 3I_2 = 6H$.

200 grammes = 6 grammes.

33·33 „ = 1 gramme = 1,000 c.c. N. solution.

0·003333 gramme = 1 c.c. N/10 „

Weigh out about 0·4 gramme of the crystals in a stoppered bottle and dissolve in sufficient water to produce 100 c.c. Take 20 c.c. and titrate as directed for potassium dichromate.

Solution of Chromic Acid.—The amount of chromic anhydride in this preparation is determined in the same way. About 1·5 grammes diluted to 100 c.c. makes a solution of convenient strength.

Potassium Dichromate.—The official salt should contain at least 99 per cent. of the pure substance. The determination is made by the iodometric method.

From the equation given on p. 91,

$K_2Cr_2O_7 = 3I_2 = 6H$.

294 grammes = 6 grammes.

49 „ = 1 gramme = 1,000 c.c. N. solution.

0·0049 gramme = 1 c.c. N/10 „

Weigh out 0·5 gramme and dissolve in sufficient water to make 100 c.c. Titrate 20 c.c. as directed on p. 91.

Calcium Hypophosphite.—This salt is readily oxidised in presence of acid in accordance with the equations

$$Ca(H_2PO_2)_2 + H_2SO_4 = CaSO_4 + 2H_3PO_2.$$
$$2H_3PO_2 + 2O_2 = 2H_3PO_4.$$

If the oxidation is carried out by means of standard potassium dichromate solution under appropriate conditions the reaction can be used for the determination of the purity of calcium hypophosphite. The salt usually contains a small amount of calcium phosphite as impurity, and as this substance is also readily oxidised, it must be

removed before the determination of hypophosphite. The removal is effected by the addition of lead acetate, lead phosphite is thrown down as a white precipitate and the more soluble lead hypophosphite remains in solution. When the precipitate has subsided an aliquot part of the clear supernatant liquid is treated with acid and an excess of standard potassium dichromate solution.

The excess of potassium dichromate is then determined by means of potassium iodide and sodium thiosulphate solution.

From the above equation

$Ca(H_2PO_2)_2 = 2O_2 = 8H.$

170 grammes = 8 grammes.

21·25 „ = 1 gramme = 1,000 c.c. N. solution.

0·02125 gramme = 1 c.c. „ „

Weigh out 2·5 grammes of the salt and dissolve it in 40 c.c. of water. Add 5 c.c. of a 10 per cent. solution of lead acetate, make the mixture up to 50 c.c. with water, shake thoroughly and set aside for the precipitate of lead phosphite to settle. Several hours may elapse before the precipitate has completely subsided, but usually after about one hour sufficient clear liquid can be withdrawn from the upper part of the mixture to proceed with the remainder of the determination.

Take 10 c.c. of the clear liquid (representing 0·5 gramme of calcium hypophosphite), add 50 c.c. of N. potassium dichromate solution and 10 c.c. of sulphuric acid; heat for one hour on the water-bath, cool and make up to 250 c.c. Take 25 c.c. of this solution (representing 0·05 gramme of calcium hypophosphite and 5 c.c. of N. potassium dichromate solution), add about 2 grammes of potassium iodide solution and titrate the liberated iodine with N/10 sodium thiosulphate solution, using starch water as indicator.

The quantity of phosphite present may be ascertained by repeating the determination with the omission of the treatment with lead acetate. The difference between the volumes of normal potassium dichromate solution used up in the two oxidation experiments represents the quantity required to oxidise the calcium phosphite, and the result is calculated from the equations

$$Ca_3(PO_3)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_3.$$
$$2H_3PO_3 + 2O = 2H_3PO_4,$$

whence $Ca_3(PO_3)_2 = 2O = 4H.$

278 grammes = 4 grammes.

69·5 „ = 1 gramme = 1,000 c.c. N. solution.

0·0695 gramme = 1 c.c. „ „

The salt should contain at least 98 per cent. of pure calcium hypophosphite.

Sodium Hypophosphite.—On account of the deliquescent character of this salt a determination of the moisture is first made by drying at 110°. The titration is then carried out with the dried salt by the method given for calcium hypophosphite.

$NaH_2PO_2 = O_2 = 4H.$
88 grammes = 4 grammes.
22 „ = 1 gramme = 1,000 c.c. N. solution.
0·022 gramme = 1 c.c. „ „

The dried salt should contain at least 97 per cent. of pure sodium hypophosphite.

Anhydrous Sodium Arsenate.—This substance is an oxidising agent and, in presence of acid, liberates iodine from potassium iodide. The changes taking place may be represented as follows :—

$$2Na_2HAsO_4 + 4HCl = As_2O_5 + 4NaCl + 3H_2O.$$
$$KI + HCl = KCl + HI.$$
$$2As_2O_5 + 8HI = As_4O_6 + 4H_2O + 4I_2.$$

It will be observed that the last equation is the reverse of the equation given on p. 81 for the oxidation of arsenious oxide by means of iodine. It is pointed out there that the reaction is reversible. When the complete oxidation of arsenious oxide is desired the reaction is made to take place in presence of sodium bicarbonate; when the complete reduction from arsenic oxide to arsenious oxide is desired an excess of acid is used.

The purity of sodium arsenate, therefore, may be determined by treating it with potassium iodide in presence of excess of hydrochloric acid and titrating the liberated iodine with standard thiosulphate solution. The reaction mixture should contain about 10 per cent. of hydrogen chloride and should be allowed to stand for ten minutes before titrating, so that the liberation of iodine may be complete. An orange-coloured precipitate of arsenious iodide appears under these conditions, but its presence does not interfere with the main reaction, and it is decomposed and redissolved as the titration proceeds. The arsenious iodide is formed in the liquid when there is a high concentration of hydriodic acid, thus :—

$$As_4O_6 + 12HI = 4AsI_3 + 6H_2O.$$

As the solution becomes more dilute during the titration the reverse reaction takes place and the arsenious oxide and hydriodic acid re-formed pass into solution. Starch water cannot be used as indicator in this determination, because it is hydrolysed by the strongly acid liquid. The disappearance of the yellow colour of the free iodine must be taken as the end-point.

From the above equation

$2Na_2HAsO_4 = 2I_2 = 4H.$
372 grammes = 4 grammes.
93 ,, = 1 gramme = 1,000 c.c. N. solution.
0·0093 gramme = 1 c.c. N/10 ,,

Weigh out about 1 gramme of the sample and dissolve it in sufficient water to make 100 c.c. Take 20 c.c., dissolve in it about 3 grammes of potassium iodide and add 20 c.c. of hydrochloric acid. Set aside for ten minutes and titrate with N/10 sodium thiosulphate solution.

At least 98 per cent. of pure anhydrous disodium hydrogen arsenate should be present.

Solution of Chlorinated Lime.—The available chlorine yielded by this solution is determined by the method described for bleaching powder (p. 90).

Weigh out about 10 grammes of the sample and dilute to 100 c.c. Take 20 c.c., add about 1 gramme of potassium iodide and a little hydrochloric acid. Titrate with N/10 sodium thiosulphate solution using starch water as indicator.

The solution should contain at least 2 per cent. of available chlorine.

Solution of Chlorinated Soda.—This solution contains sodium chloride and hypochlorite. When treated with an acid, interaction takes place with liberation of chlorine, thus :—

$$NaOCl + NaCl + H_2SO_4 = Cl_2 + Na_2SO_4 + H_2O.$$

This available chlorine is determined exactly as described for solution of chlorinated lime.

At least 2·5 per cent. of available chlorine should be present.

Sulphurous Acid.—The acid of the British Pharmacopœia should contain 6·4 per cent. of hydrogen sulphite or 5 per cent. of sulphur dioxide.

From the equation

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI,$$

$H_2SO_3 = SO_2 = I_2 = 2H.$
82 grammes = 64 grammes = 2 grammes.
41 ,, = 32 ,, = 1 gramme = 1,000 c.c. N. sol.
0·0041 gramme = 0·0032 gramme = 1 c.c. N/10 ,,

Weigh out 1 gramme of the acid and add it to 30 c.c. of N/10 iodine solution. Dilute the solution well and titrate the excess of iodine with N/10 sodium thiosulphate solution, using starch water as indicator.

Sodium Sulphite.—The official salt is required to contain at least 94 per cent. of the pure crystalline hydrate $Na_2SO_37H_2O$. It is

readily oxidised by iodine to sodium sulphate. Accurate results are not obtained by direct titration with iodine solution because the salt in aqueous solution is rapidly oxidised by the air. The crystals should be dissolved in the iodine solution and the excess titrated with standard sodium thiosulphate solution.

From the equation

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI,$$

$Na_2SO_37H_2O = I_2 = 2H.$

252 grammes = 2 grammes.

126 ,, = 1 gramme = 1,000 c.c. N. solution.

0·0126 gramme = 1 c.c. N/10 ,,

Weigh out 0·5 gramme and dissolve in 80 c.c. of N/10 iodine solution. Dilute to 100 c.c. and titrate 20 c.c. with N/10 sodium thiosulphate solution, using starch water as indicator. The reading of thiosulphate solution deducted from 16 c.c. gives the volume of N/10 iodine solution required to oxidise 0·1 gramme of the sample.

Sulphites in Glucose.—Glucose usually contains small quantities of sulphites, but the amount present should not exceed 0·1025 per cent. calculated as sulphur dioxide SO_2.

The determination is made as directed for sulphurous acid.

Weigh out about 10 grammes of the sample and add it to a mixture of 10 c.c. of N/10 iodine solution and 100 c.c. of water; shake until mixed, and titrate back immediately with N/10 sodium thiosulphate solution, using starch water as indicator. The mixture must not be allowed to stand before titrating back or some iodine is reduced by the glucose.

Solution of Formaldehyde.—As mentioned on p. 55, the quantitative oxidation of formaldehyde to formic acid by standard iodine may be used for the determination of formaldehyde.

The solution is mixed with an excess of standard iodine solution, and sodium hydroxide is added to convert the iodine into sodium iodide and iodate (*see* equations on p. 82). The oxidation is complete after standing for ten minutes, and the iodine is then liberated again by adding excess of hydrochloric acid, thus :—

$$5NaI + NaIO_3 + 6HCl = 3I_2 + 6NaCl + 3H_2O.$$

The iodine set free is then titrated with standard sodium thiosulphate solution.

From the above equation

$HCHO = I_2 = 2H.$

30 grammes = 2 grammes.

15 ,, = 1 gramme = 1,000 c.c. N. solution.

0·0015 gramme = 1 c.c. N/10 ,,

Weigh out about 2 grammes of the sample and dilute to 100 c.c. Take 10 c.c. of the diluted solution, add 100 c.c. of N/10 iodine solution, and then sodium hydroxide solution drop by drop until a clear yellow colour remains. Set aside for ten minutes at room temperature, acidify with hydrochloric acid, and titrate the iodine in excess by means of N/10 sodium thiosulphate solution.

This process is accurate if pure formaldehyde is present. Acetaldehyde and acetone use up iodine by the formation of iodoform, and certain other aldehydes are oxidised by iodine solution. The presence of these impurities therefore vitiates the result.

CHAPTER XI

PRECIPITATION REACTIONS

Silver Nitrate.

Solutions of silver nitrate react quantitatively with solutions of several salts, precipitating the insoluble silver salts. A standard solution of silver nitrate may therefore be used as a means of determining these salts, which include :—chlorides, bromides, iodides, cyanides, and thiocyanates.

The reaction between silver nitrate and sodium chloride is represented by the equation

$$AgNO_3 + NaCl = AgCl + NaNO_3,$$

whence $AgNO_3 = Cl = H$.

$$170 \text{ grammes } = 1 \text{ gramme} = 1{,}000 \text{ c.c. N. sol.}$$

A decinormal solution is most commonly used.

Weigh out 17 grammes of recrystallised silver nitrate and dissolve in sufficient water to make 1,000 c.c.

Standardisation by means of Sodium Chloride.

The silver nitrate solution is added from the burette to the standard sodium chloride solution until all the chloride is precipitated as silver chloride. To indicate the termination of the reaction, potassium chromate is added. The least excess of silver nitrate over the

amount required to react with the chloride is indicated by the appearance of a red colour, due to the precipitation of silver chromate, thus :—

$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3.$$

The red colour shows up well against the white precipitate of silver chloride, especially by artificial light. The solutions must not contain free acid, as silver chromate is not precipitated from acid solutions. The silver solution should be added slowly, or a curdy precipitate of silver chromate, which is not readily decomposed by the sodium chloride solution, may be formed before all the chloride is precipitated.

Pure sodium chloride is not readily obtained by the ordinary process of crystallisation as it is almost equally soluble in hot and cold water. It is, however, much less soluble in strong hydrochloric acid than in water, and pure sodium chloride is precipitated when a current of hydrogen chloride gas is passed into a strong solution of the impure salt. The precipitate is collected, washed with a little water, and dried in the steam-oven.

From the above equation

$$NaCl \quad = H.$$

58·5 grammes = 1 gramme = 1,000 c.c. N. solution.

Prepare a N/10 solution by dissolving 0·585 gramme of the pure salt in water and diluting to 100 c.c.

Take 20 c.c., add a few drops of potassium chromate solution, and run in the silver nitrate solution until the precipitate is tinged pink. The approach of the end-point is shown by the sudden aggregation of the precipitate into curds just before the appearance of the pink colour.

Standardisation by means of N/10 Hydrochloric Acid.

Silver nitrate solution may be standardised against a N/10 solution of hydrochloric acid. In order that potassium chromate may be used as indicator the acid must be neutralised. This may be done by adding sodium hydroxide solution until the liquid is neutral to litmus paper. An excess of alkali must be avoided as it decomposes silver nitrate. A better way is to add excess of calcium carbonate, which must be free from chloride. The acid is completely converted into calcium chloride and the excess of calcium carbonate, being insoluble, does not affect silver nitrate.

The factor of the silver nitrate solution is calculated as usual.

Bromides and Iodides.

Other haloid salts act upon silver nitrate in the same way as chlorides. Bromides and iodides may be determined by titration with standard silver nitrate solution.

For practice find the purity of ammonium bromide. The reaction with silver nitrate is expressed by the equation

$AgNO_3 + NH_4Br = AgBr + NH_4NO_3$.

$NH_4Br = AgNO_3 = H$.

98 grammes = 1 gramme = 1,000 c.c. N. solution.

0·0098 gramme = 1 c.c. N/10 „

Take about 0·8 gramme of the sample, dissolve it in water, and dilute to 100 c.c. Titrate 20 c.c. with N/10 silver nitrate, using potassium chromate as indicator.

This salt is somewhat hygroscopic, and on this account the British Pharmacopœia directs that the moisture present should be deter-

mined by drying at 100°, and the dried salt used for the titration. The dried salt should contain at least 98 per cent. of pure ammonium bromide.

Determination of Silver.

Silver may be determined by means of sodium chloride as described above, provided that the solution contains no free acid. Acid solutions of silver may be titrated with standard sodium chloride solution, the end of the reaction being indicated when no further precipitation takes place on the addition of more sodium chloride solution. The precipitate settles very slowly, however, and the process is tedious. For the determination of silver in acid solution the thiocyanate method described in Chapter XII. is to be preferred.

Potassium Cyanide.

When excess of silver nitrate is added to a solution of potassium cyanide, silver cyanide is precipitated according to the equation

$$AgNO_3 + KCN = AgCN + KNO_3.$$

If the silver nitrate solution is added gradually, this reaction may be shown to take place in two stages. Potassium argenticyanide is first formed, thus :—

$$AgNO_3 + 2KCN = KAg(CN)_2 + KNO_3 \qquad (1)$$

This compound is soluble in water and the solution remains clear. If now a further quantity of silver nitrate solution is added, silver cyanide is precipitated, thus :—

$$KAg(CN)_2 + AgNO_3 = 2AgCN + KNO_3 \qquad (2)$$

On running silver nitrate into potassium cyanide solution the first appearance of a precipitate indicates the commencement of reaction (2) and the termination of

reaction (1). The reading is taken when the solution becomes cloudy, and the result is calculated from equation (1).

Owing to the poisonous nature of cyanides, the solutions should never be measured in a pipette, but should always be weighed.

$2KCN = AgNO_3 = H.$

130 grammes = 1 gramme = 1,000 c.c. N. solution.

0·013 gramme = 1 c.c. N/10 ,,

Weigh out about 0·25 gramme of potassium cyanide, dissolve in about 100 c.c. of water, and titrate with N/10 silver nitrate solution until a permanent cloudiness appears.

Diluted Hydrobromic Acid.—In addition to the acidimetric determination described on p. 41, the strength of hydrobromic acid must be checked by titration with standard silver nitrate solution. The acid must be neutralised with calcium carbonate, thus :—

$$CaCO_3 + 2HBr = CaBr_2 + H_2O + CO_2.$$

$$CaBr_2 + 2AgNO_3 = Ca(NO_3)_2 + 2AgBr,$$

whence $HBr = AgNO_3 = H.$

81 grammes = 1 gramme = 1,000 c.c. N. solution.

0·0081 gramme = 1 c.c. N/10 ,,

Weigh out about 8 grammes of the acid and dilute to 100 c.c. Take 20 c.c., add excess of calcium carbonate, and titrate with N/10 silver nitrate solution, using potassium chromate as indicator.

The results obtained by this method and by titration with sodium hydroxide should be the same, showing the absence of other acids and of bromides.

Hydrochloric Acid.—The strength of hydrochloric acid and diluted hydrochloric acid should be checked by means of silver nitrate in the same way as hydrobromic acid.

One gramme of the concentrated acid or 3 grammes of the diluted acid made up to 100 c.c. forms a suitable solution for titration with N/10 silver nitrate solution.

Potassium Bromide and Iodide.—Owing to the tendency of these two salts to contain hygrosopic water, a determination of moisture is made before titrating, by drying at 100°. After drying potassium

bromide should contain 98 per cent. and potassium iodide 99 per cent. of the pure salt. The purity is determined as for ammonium bromide.

$$KBr + AgNO_3 = AgBr + KNO_3$$
$$KI + AgNO_3 = AgI + KNO_3$$

KBr = KI = H.
119 grammes = 166 grammes = 1 gramme = 1,000 c.c. N. solution.
0·0119 gramme = 0·0166 gramme = 1 c.c. N/10 solution.

About 1·5 grammes of either of the dried salts dissolved in sufficient water to make 100 c.c. forms a solution of convenient strength for titration with N/10 silver nitrate solution.

Sodium Bromide and Iodide.—These two salts are hygroscopic, and a determination of moisture is made by drying at 110°. In each case the dried salt should contain at least 99 per cent. of the pure compound. The determination is made in the same way as for ammonium bromide.

$$NaBr + AgNO_3 = AgBr + NaNO_3$$
$$NaI + AgNO_3 = AgI + NaNO_3$$

NaBr = NaI = H.
103 grammes = 150 grammes = 1 gramme = 1,000 c.c. N. solution.
0·0103 gramme = 0·015 gramme = 1 c.c. N/10 solution.

About 1·5 grammes of either salt after drying may be dissolved in sufficient water to produce 100 c.c., for titration with N/10 silver nitrate solution.

Strontium Bromide.—This salt is required to contain not less than 97 per cent. of the crystalline substance $SrBr_2.6H_2O$. It reacts with silver nitrate in the same way as the other soluble bromides.

From the equation

$$SrBr_2 + 2AgNO_3 = Sr(NO_3)_2 + 2AgBr.$$

$SrBr_2.6H_2O = 2AgNO_3 = 2H.$
355·5 grammes = 2 grammes.
177·75 „ = 1 gramme = 1,000 c.c. N. solution.
0·01775 gramme = 1 c.c. N/10 „

Weigh out about 2 grammes and proceed as directed for ammonium bromide.

Diluted Hydrocyanic Acid.—The acid of the British Pharmacopœia should contain 2 per cent. of hydrogen cyanide, HCN.

The method described for the determination of potassium cyanide may be used, with slight modification, for hydrocyanic acid. The acid must be neutralised because silver cyanide is not soluble in hydro-

cyanic acid, the compound $HAg(CN)_2$ being unstable. The neutralisation is effected by adding excess of solution of ammonia, and a little potassium iodide is used as indicator. Silver cyanide is soluble in solution of ammonia, and therefore the precipitation of silver cyanide which indicates the termination of reaction (1) on p. 104 does not take place. In presence of potassium iodide the complete conversion of the cyanide into argenticyanide is indicated by the immediate precipitation of silver iodide, which is insoluble in solution of ammonia but is not precipitated so long as any cyanide remains uncombined with silver.

The hydrocyanic acid must be weighed. The use of a pipette is dangerous, owing to the poisonous nature of the vapour given off.

From the equations

$$HCN + NH_4OH = NH_4CN + H_2O.$$

$$2NH_4CN + AgNO_3 = NH_4Ag(CN)_2 + NH_4NO_3.$$

$$2HCN = AgNO_3 = H.$$

54 grammes = 1 gramme = 1,000 c.c. N. solution.

0·0054 gramme = 1 c.c. N/10 ,,

Weigh out about 5 grammes of the sample in a stoppered bottle. Transfer to the titrating flask, add about 50 c.c. of water, 5 c.c. of 10 per cent. solution of ammonia and a few drops of 10 per cent. solution of potassium iodide. Titrate with N/10 silver nitrate solution until a permanent cloudiness appears.

Cherry-laurel Water.—The essential constituent of this preparation is hydrocyanic acid, of which 0·1 per cent. should be present. The determination is carried out exactly as for hydrocyanic acid except that N/100 silver nitrate should be used.

About 10 grammes may be weighed out for each titration.

Chloral Hydrate.—Sodium hydroxide decomposes chloral hydrate in the cold with formation of chloroform, but if the substances are heated together in a closed vessel the chloroform is decomposed with production of sodium chloride and formate. The decomposition of chloral hydrate under these conditions is expressed by the equation

$$CCl_3CH(OH)_2 + 5NaOH = 3NaCl + 2HCOONa + 3H_2O.$$

The reaction is quantitative, and by determining the sodium chloride with standard silver nitrate solution the purity of the chloral hydrate can be ascertained.

From the above equation

$$CCl_3CH(OH)_2 = 3NaCl = 3H.$$

165·5 grammes = 3 grammes.

55·16 ,, = 1 gramme = 1,000 c.c. N. solution.

0·005516 gramme = 1 c.c. N/10 ,,

Weigh 0·1 gramme of the sample into a strong bottle, add 10 c.c. of alcohol, and shake till dissolved. Add 10 c.c. of N.NaOH, and close the bottle with a rubber stopper, fastening it securely down with string or wire. Heat in the water-bath for three hours, then neutralise with dilute sulphuric acid, using phenol-phthalein as indicator, and titrate with N/10 silver nitrate solution, using potassium chromate as indicator.

CHAPTER XII

PRECIPITATION REACTIONS (*continued*)

Standard Thiocyanate Solution.

Ammonium thiocyanate * reacts with silver nitrate to form a white precipitate of silver thiocyanate. The precipitation is complete even in presence of a large amount of nitric acid.

The reaction is expressed by the equation

$$AgNO_3 + NH_4SCN = AgSCN + NH_4NO_3,$$

whence

$NH_4SCN = AgNO_3 = H.$

76 grammes $= 1$ gramme $= 1{,}000$ c.c. N. sol.

The salt is hygroscopic and a standard solution cannot be prepared by dissolving a weighed amount in water. The solution must be standardised by means of silver nitrate solution. The indicator used is ferric sulphate, which reacts with the thiocyanate, giving a deep-red solution of ferric thiocyanate, thus :—

$$Fe_2(SO_4)_3 + 6NH_4SCN = 2Fe(SCN)_3 + 3(NH_4)_2SO_4.$$

To make an approximately decinormal solution, weigh out 8 grammes of the salt and dissolve in sufficient water to produce 1,000 c.c.

Take 20 c.c. of N/10 silver nitrate solution, dilute

* Potassium thiocyanate can be used equally well.

well with water, add a few c.c. of dilute nitric acid and 5 c.c. of a saturated solution of iron alum or a little solution of ferric sulphate. Run in the thiocyanate solution from the burette, with constant shaking, until the end of the reaction is shown by the appearance of a permanent colour. Care must be taken not to carry the titration too far. The appearance of a pink tint which does not disappear on stirring is the end-point to be looked for. A deep red colour indicates over-titration. The appearance of the colour is most readily seen if a white porcelain vessel is used for the titration.

The factor of the thiocyanate solution is then calculated in the usual way.

Determination of Silver.

For practice, determine the proportion of silver in an alloy of copper and silver.

Take about 0·25 gramme of the alloy and dissolve in warm nitric acid. Heat until no more brown fumes are expelled and dilute well with water, add 5 c.c. of saturated iron alum solution as indicator, and titrate with N/10 ammonium thiocyanate solution.

1 c.c. N/10 thiocyanate solution = 0·0108 gramme of silver.

Determination of Halides.

The standard thiocyanate solution may be used for the determination of chlorides, bromides and iodides, by a process of residual titration requiring the use of a standard solution of silver nitrate. Nitric acid and an excess of the silver nitrate solution are added to the solution of the haloid salt, and the silver nitrate not precipitated is determined by titration with standard

thiocyanate solution. This method has the advantage over a direct titration with silver nitrate that it may be used in cases where the presence of free acid is necessary. When using the method for the determination of chlorides it is better to filter off the precipitate of silver chloride before titrating back, since interaction takes place between ammonium thiocyanate and silver chloride. In the determination of bromides or iodides there appears to be little or no interaction between the silver halide and ammonium thiocyanate and filtration is usually regarded as unnecessary.

Diluted Hydriodic Acid.—This preparation should contain 10 per cent. of hydrogen iodide and 1 per cent. of hypophosphorous acid. The strength is determined by the method of residual titration referred to on p. 110. The direct titration with silver nitrate solution, using potassium chromate as indicator, is not applicable because in the absence of nitric acid the hypophosphorous acid reduces silver nitrate with precipitation of metallic silver.

$HI + AgNO_3 = AgI + HNO_3.$
$HI = AgNO_3 = H.$
128 grammes = 1 gramme = 1,000 c.c. N. solution.
0·0128 gramme = 1 c.c. N/10 „

Weigh out 5 grammes of the acid, add a little nitric acid and 50 c.c. of N/10 silver solution. Then titrate back with N/10 ammonium thiocyanate solution, using ferric sulphate as indicator.

Syrup of Ferrous Iodide.—A direct titration of the iodide in this preparation by means of silver nitrate solution is not possible because the indicator, potassium chromate, reacts with ferrous iodide, precipitating ferrous chromate. Further, the glucose present in the syrup is a reducing agent and would give rise to inaccuracy. The method of residual titration, using silver nitrate and ammonium thiocyanate, gives good results.

From the equation

$FeI_2 + 2AgNO_3 = Fe(NO_3)_2 + 2AgI.$
$FeI_2 = 2AgNO_3 = 2H.$
310 grammes = 2 grammes.
155 „ = 1 gramme = 1,000 c.c. N. solution.
0·0155 gramme = 1 c.c. N/10 „

Weigh out about 5 grammes of the syrup and mix with 20 c.c. of water, add nitric acid and 30 c.c. of N/10 silver nitrate solution; then titrate back with N/10 ammonium thiocyanate solution, using ferric sulphate as indicator.

Volatile Oil of Mustard.—The principal constituent of this oil is allyl isothiocyanate. This substance, when heated with silver nitrate in presence of ammonia, is decomposed in the following way :—

$$C_3H_5NCS + 3NH_3 + 2AgNO_3 = Ag_2S + C_3H_5NCNH + 2NH_4NO_3.$$

For the determination of allyl isothiocyanate an alcoholic solution of the oil is heated with an excess of standard silver nitrate solution and ammonia; the precipitate of silver sulphide is filtered off and the excess of silver nitrate is determined by titration with standard potassium thiocyanate solution.

From the above equation

$C_3H_5NCS = 2AgNO_3 = 2H.$
99 grammes = 2 grammes.
49·5 ,, = 1 gramme = 1,000 c.c. N. solution.
0·00495 gramme = 1 c.c. N/10 ,,

Weigh out about 1 gramme of the oil and dissolve in such a quantity of alcohol that 50 c.c. of the solution contain exactly 1 gramme of oil. Measure 5 c.c. of the solution into a 100 c.c. flask, add 30 c.c. of N/10 silver nitrate solution and 5 c.c. of solution of ammonia. Maintain at a temperature of 80° for half an hour by heating on the water-bath, shaking frequently. Cool to 15·5°, dilute to 100 c.c. with water, and filter. Take 50 c.c. of the filtrate, add 4 c.c. of concentrated nitric acid, and titrate with N/10 potassium thiocyanate solution, using ferric sulphate as indicator.

The oil should contain at least 92 per cent. of allyl isothiocyanate.

Yellow Mercuric Oxide.—Solutions of mercuric nitrate react quantitatively with ammonium thiocyanate in the same way as silver nitrate, forming mercuric thiocyanate and ammonium nitrate, thus:

$$Hg(NO_3)_2 + 2NH_4SCN = Hg(SCN)_2 + 2NH_4NO_3.$$

The mercuric thiocyanate, however, is not immediately precipitated in the presence of excess of nitric acid, and the solution remains clear until near the end of the titration.

This reaction is used for determining the purity of mercuric oxide, which should contain at least 99·3 per cent. of the pure substance. The oxide is dissolved in excess of nitric acid and the solution is titrated with standard thiocyanate solution:

$$HgO + 2HNO_3 = Hg(NO_3)_2 + H_2O$$

whence $HgO = 2NH_4SCN = 2H$.

216·5 grammes = 2 grammes.

108·25 „ = 1 gramme = 1,000 c.c. N. solution.

0·010825 gramme = 1 c.c. N/10 „

Weigh out 1 gramme of the sample, dissolve it in about 5 c.c. of nitric acid and dilute to 100 c.c. Take 20 c.c. and titrate with N/10 solution of ammonium thiocyanate, using solution of ferric sulphate as indicator.

Red Mercuric Oxide should contain at least 99·3 per cent. of the pure substance. The purity is determined in the same way as for the yellow oxide.

CHAPTER XIII

MISCELLANEOUS EXERCISES

When two substances occur together in a mixture or solution it is possible in many cases to determine the amounts present by the use of two volumetric solutions.

If the two substances are of dissimilar chemical character, as with, say, a solution of potassium hydroxide and potassium oxalate or sulphuric acid and sodium chloride, each substance may be determined by the ordinary method independently of the other. When the two substances possess some property in common upon which the sole means of determining one of them depends, the method becomes somewhat more complicated.

A number of exercises of this kind may be devised and a few typical examples are given here.

These determinations may be carried out with standard solutions of any convenient strength, but the calculation of the result becomes a little involved in some cases unless solutions are used which bear some definite relation to the normal standard.

Potassium Oxalate and Oxalic Acid.

Both these substances are oxidised by potassium permanganate in presence of sulphuric acid, but only

the oxalic acid reacts with alkali. The determination is therefore carried out in the following way :—

Dissolve a weighed amount of the mixture in sufficient water to make 100 c.c. Titrate 20 c.c. with N/10 sodium hydroxide solution, using phenol-phthalein as indicator. Add excess of sulphuric acid and titrate in the usual way with N/10 potassium permanganate solution. The difference between the two readings gives the volume of N/10 potassium permanganate required to oxidise the potassium oxalate in 20 c.c. of the solution. The amount of oxalic acid is calculated from the reading of sodium hydroxide solution.

Sulphuric and Oxalic Acids.

Both these substances may be determined by means of standard alkali, but only the oxalic acid reduces potassium permanganate. The method of determination is to titrate with N/10 sodium hydroxide solution, using phenol-phthalein as indicator, then to add sulphuric acid and titrate with N/10 potassium permanganate solution. The difference between the two readings gives the N/10 sodium hydroxide solution required to neutralise the sulphuric acid, while the oxalic acid is calculated in the usual way from the reading of potassium permanganate solution.

Sulphuric and Hydrochloric Acids.

The reading for total acid is found by means of N/10 sodium hydroxide solution, and the reading for hydrochloric acid by means of N/10 silver nitrate solution. From the difference between the two readings the sulphuric acid is calculated.

Sulphuric and Phosphoric Acids.

The determination may be made by titrating with standard sodium hydroxide solution, using first methyl orange and then phenol-phthalein as indicator. The reaction with methyl orange is given when the sulphuric acid has been completely neutralised and the phosphoric acid has been converted into sodium dihydrogen phosphate. The additional alkali required to make the solution neutral to phenol-phthalein is that required to convert the sodium dihydrogen phosphate into disodium hydrogen phosphate, and from this reading the amount of phosphoric acid present is calculated. This additional reading deducted from the reading with methyl orange gives the alkali necessary to neutralise the sulphuric acid.

Sodium Chloride and Hydrochloric Acid.

The solution is titrated first with N/10 sodium hydroxide solution for the free acid, then with N/10 silver nitrate solution for the total chloride. From the difference between the two readings the sodium chloride is calculated.

Ferrous and Ferric Iron.

The ferrous iron is determined by titration with potassium dichromate or permanganate solution, then the total iron is found by one of the methods given for the determination of ferric salts (*see* pp. 62, 92). The difference between the two gives the ferric iron.

It may be mentioned here that instead of zinc and sulphuric acid, a solution of stannous chloride or

ammonium bisulphite may be used as reducing agent in the determination of ferric iron. For details of these methods the student is referred to larger works.

Solution of Potassium Hydroxide and Ammonia.

The total alkali is found by titration with N/10 acid. Another portion of the solution is boiled well to expel the ammonia, and the potassium hydroxide is then determined by means of N/10 acid. From the difference between the two readings the amount of ammonia present is calculated.

Ammonium Sulphate and Ammonium Chloride.

Both these salts are decomposed by sodium hydroxide and may be determined by the methods already described (p. 47); the chloride may be determined by means of standard silver nitrate solution. The volume of N. sodium hydroxide solution necessary to decompose both salts or the volume of N. sulphuric acid necessary to neutralise the ammonia evolved from both salts, is first determined, using, say, 20 c.c. of the solution. A titration of the ammonium chloride is then made by means of N/10 silver nitrate solution, using a convenient quantity of the solution of ammonium salts. From this titration the volume of N. solution necessary to react with the ammonium chloride in 20 c.c. is calculated, and the difference between this figure and the volume of N. solution equivalent to both salts gives the volume of N. solution required by the ammonium sulphate.

Boric Acid and Borax.

The borax is first determined by titration with N/10 sulphuric acid, using methyl orange as indicator. The

whole of the boric acid is now in the free state, and the amount is found by titrating with N/10 sodium hydroxide solution, using phenol-phthalein as indicator and adding sufficient glycerine to form 30 per cent. of the final volume. Twice the reading of N/10 acid deducted from the reading of N/10 alkali gives the volume of N/10 sodium hydroxide solution required by the boric acid originally present in the free state.

Available Oxygen.

It is often convenient to express the strength of an oxidising substance or solution in terms of "available oxygen," *i.e.*, the oxygen which takes part in an oxidising action. The determination in the case of potassium chromate or dichromate or chromic acid may be made by means of a standard solution of ferrous iron or by adding potassium iodide and sulphuric acid and titrating with standard sodium thiosulphate solution; for potassium permanganate either of these methods may be used or it may be titrated against a standard solution of oxalic acid. In all cases 1 c.c. of a decinormal solution of the reducing agent employed corresponds to 0·0008 gramme of available oxygen.

Sodium Hydrogen Oxalate and Potassium Hydrogen Oxalate.

These two substances present exceptions to the rule that equal volumes of all normal solutions are equivalent. They are acid salts and may be determined by titration with standard sodium hydroxide solution; they also liberate oxalic acid when treated with sulphuric acid,

and so may be determined with standard potassium permanganate solution.

In the first case

$NaHC_2O_4 + NaOH = Na_2C_2O_4 + H_2O$,

$NaHC_2O_4 = NaOH = H$.

112 grammes $= 1$ gramme $= 1{,}000$ c.c. N. sol.

In the second case

$NaHC_2O_4 + H_2SO_4 = NaHSO_4 + H_2C_2O_4$,

and $5H_2C_2O_4 = 2KMnO_4$,

$5NaHC_2O_4 = 2KMnO_4 = 10H$.

560 grammes $= 10$ grammes.

56 ,, $= 1$ gramme $= 1{,}000$ c.c. N. sol.

The normal solution of either of these salts for use with sodium hydroxide is thus twice the strength of that calculated from the reaction with potassium permanganate. This emphasises the necessity for considering in every case the reaction in which a substance takes part, when deciding how much is necessary to make 1,000 c.c. of a N. solution.

ATOMIC WEIGHTS.

		International. 1921.	Approximate.
Antimony	Sb	120·2	120
Arsenic	As	74·96	75
Barium	Ba	137·37	137·5
Boron	B	10·9	11
Bromine	Br	79·92	80
Calcium	Ca	40·07	40
Carbon	C	12·005	12
Chlorine	Cl	35·46	35·5
Chromium	Cr	52·0	52
Copper	Cu	63·57	63·5
Hydrogen	H	1·008	1
Iodine	I	126·92	127
Iron	Fe	55·84	56
Lead	Pb	207·20	207
Lithium	Li	6·94	7
Manganese	Mn	54·93	55
Mercury	Hg	200·6	200·5
Nitrogen	N	14·008	14
Oxygen	O	16·0	16
Phosphorus	P	31·04	31
Potassium	K	39·1	39
Silver	Ag	107·88	108
Sodium	Na	23·0	23
Strontium	Sr	87·63	87·5
Sulphur	S	32·06	32
Zinc	Zn	65·37	65·5

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